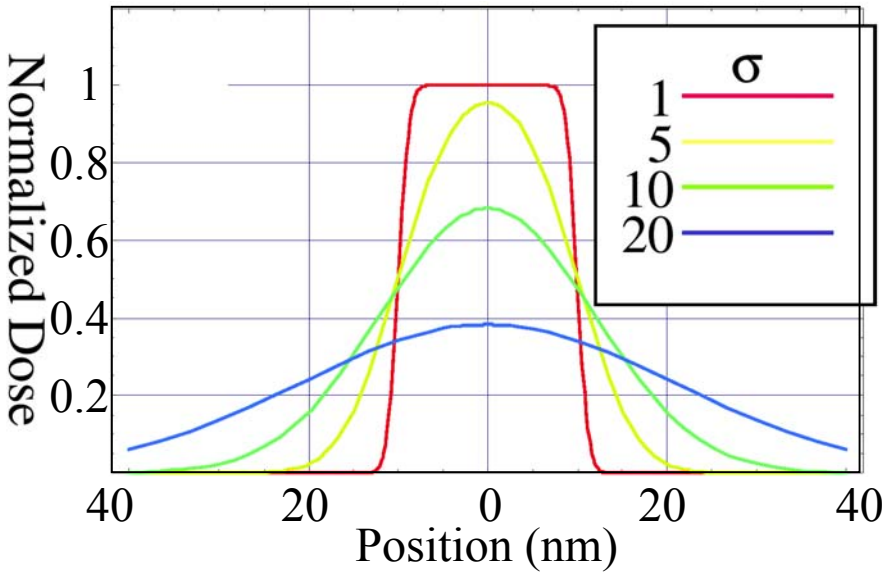
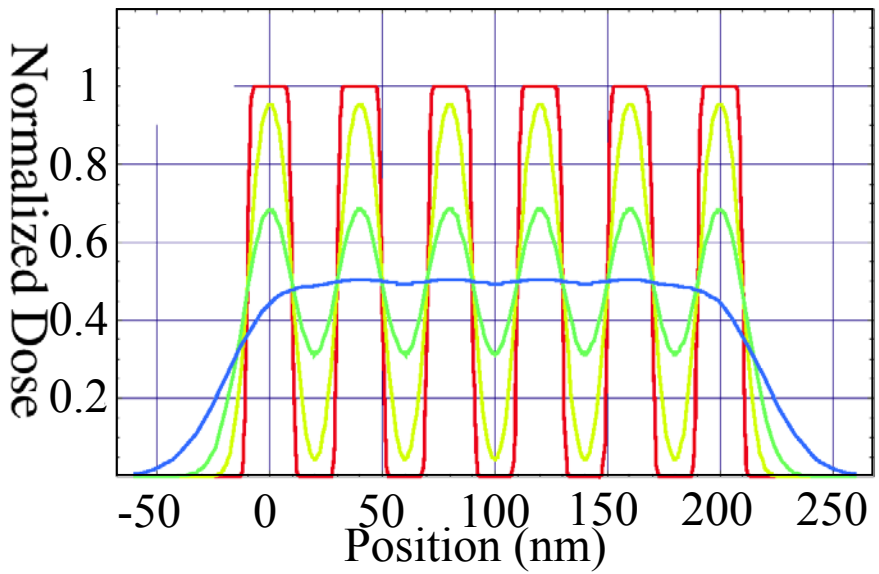
Resist Materials II

- Resolution
  - Aerial Image
    - Dose latitude
  - Statistical considerations
    - Sensitivity Limits
  - Energy Deposition Distribution
    - Beam broadening
    - Energy and chemistry
  - Development
    - Diffusion in CA materials
    - Line edge roughness
  - Limits to resolution

Resolution – Aerial Image



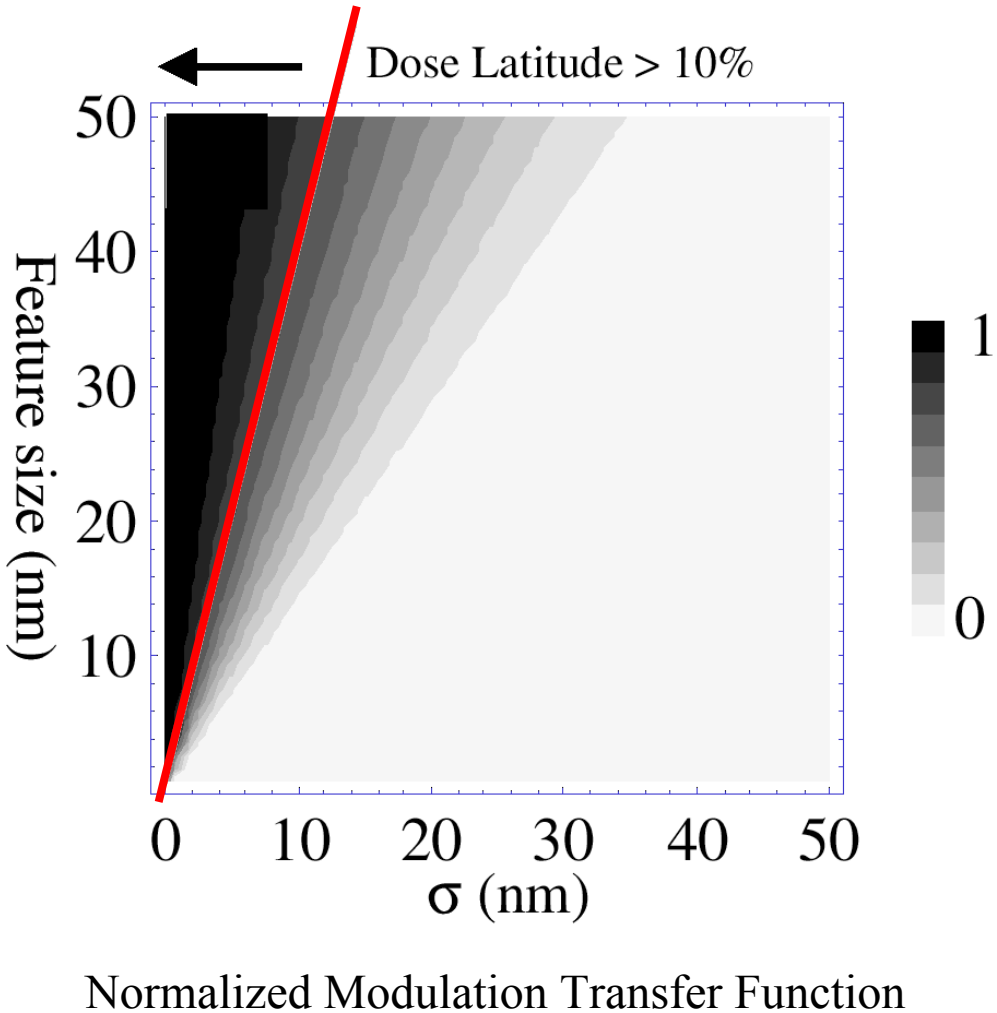
20 nm isolated feature



20 nm lines & spaces

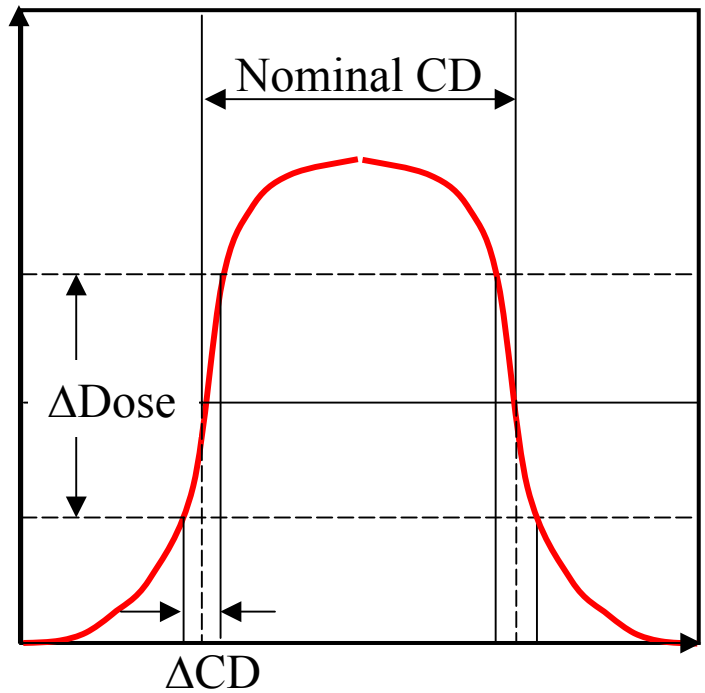
- The **aerial image** represents the intensity distribution that can be formed by a lithography system
  - Refers to energy distribution immediately above the resist surface, before any interaction with resist or substrate
- Aerial image resolution affects printable feature size
  - Modulation falls to ≈ zero when $\sigma > \sqrt{2Ln2}$ feature size

Dose Latitude



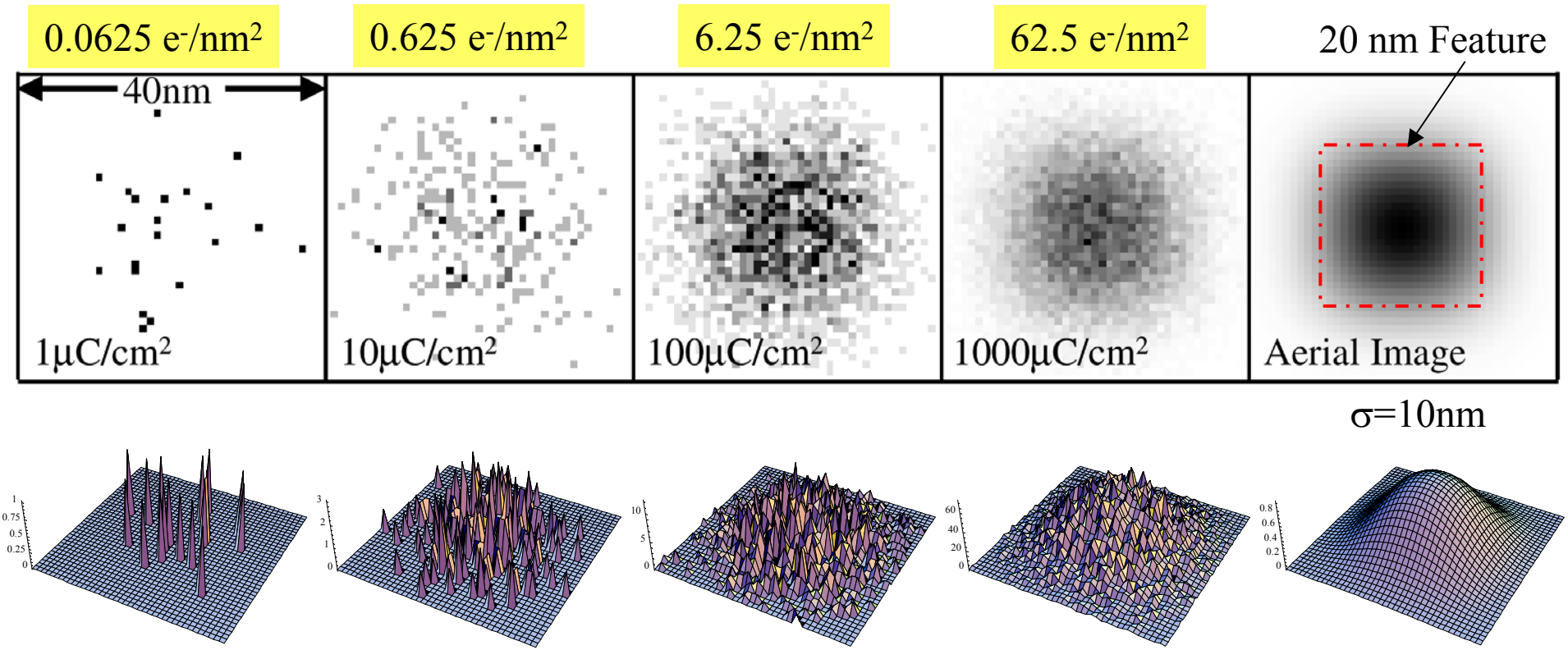
Normalized Modulation Transfer Function

- Robust process requires dose latitude (ΔDose ±10%ΔCD) > 10%
  - Blur (σ) < 20% CD



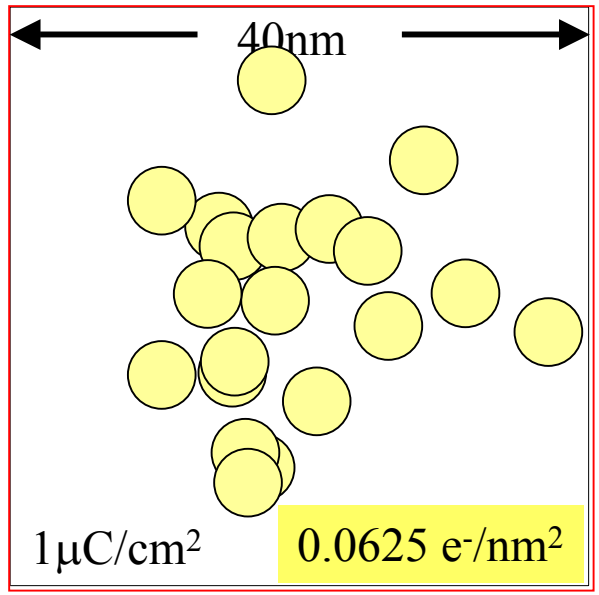
Resolution - Statistics I

- High sensitivity ➤ small numbers of electrons
- Exposure statistics can lead to large variations in feature size



Resolution - Statistics II

- Simple calculation: each electron exposes cylinder of material
  - Resolution = mean separation between electrons, δ
  - 1 μC/cm^2 ➢ δ = 4 nm
- Electrons in a bucket: probability feature fails to print < 10^{-15}
  - Feature fails to print if dose is < 0.5 dose to print on size
  - Probability is < 10^{-15} when number of electrons > 200
  - Dose = 8 μC/cm^2 for 20 nm features
- Signal to noise: √N/N < X% - what is X?



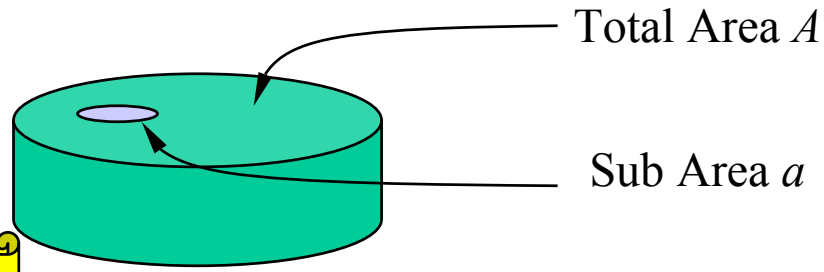
Shot-noise - Poisson Statistics

Example

Let Intensity = defocus tophat in projection electron system

35nm diameter and 4μC/cm^2

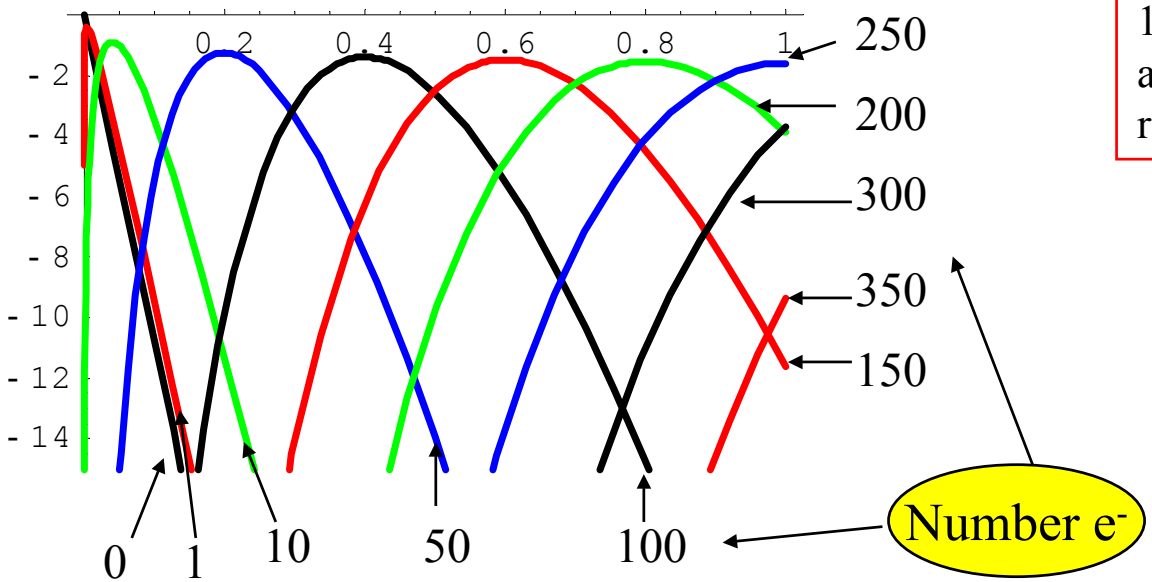
⇒ IAt = 250 electrons



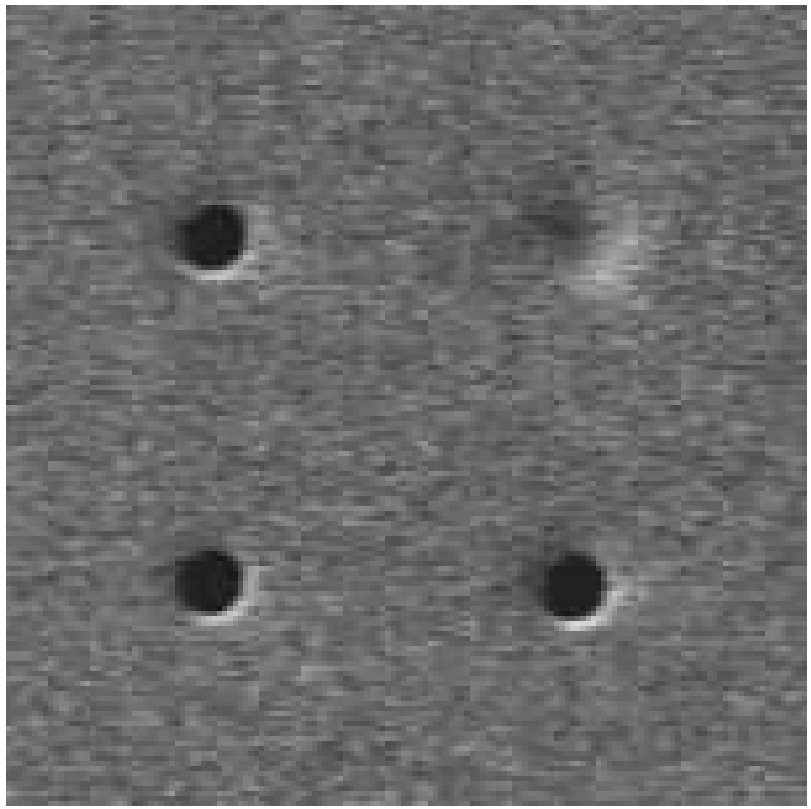
(Nominal dose to print on size = 2 x dose to clear)

Chance of getting ≤ half (Nominal Dose) is << 10^{-15}, i.e. features will always print & dose is relatively uniform

Log of the Probability to get n particles in the given area fraction



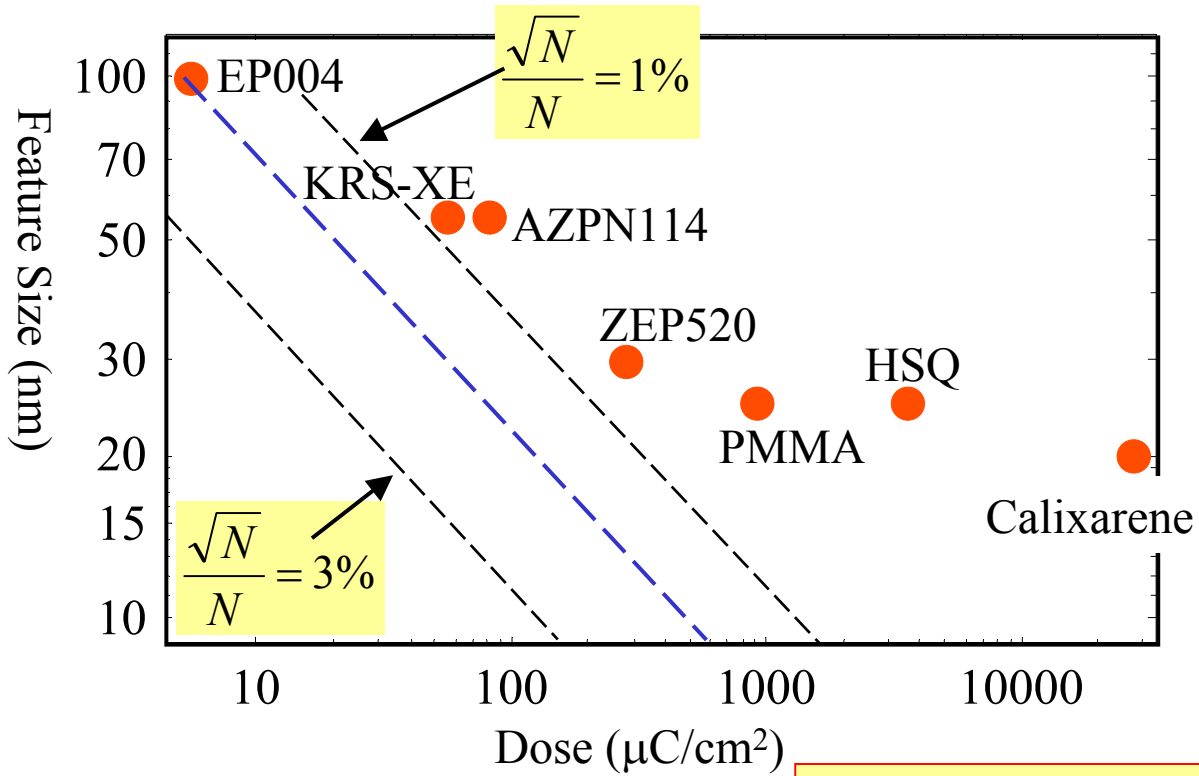
Missing Via



This is what a missing via looks like.
- In this case it mostly likely results from chemical contamination.

Observed Resolution vs Dose

$$N = \frac{Dose \cdot L^2}{e} \Rightarrow L = \sqrt{\frac{eN}{Dose}}$$

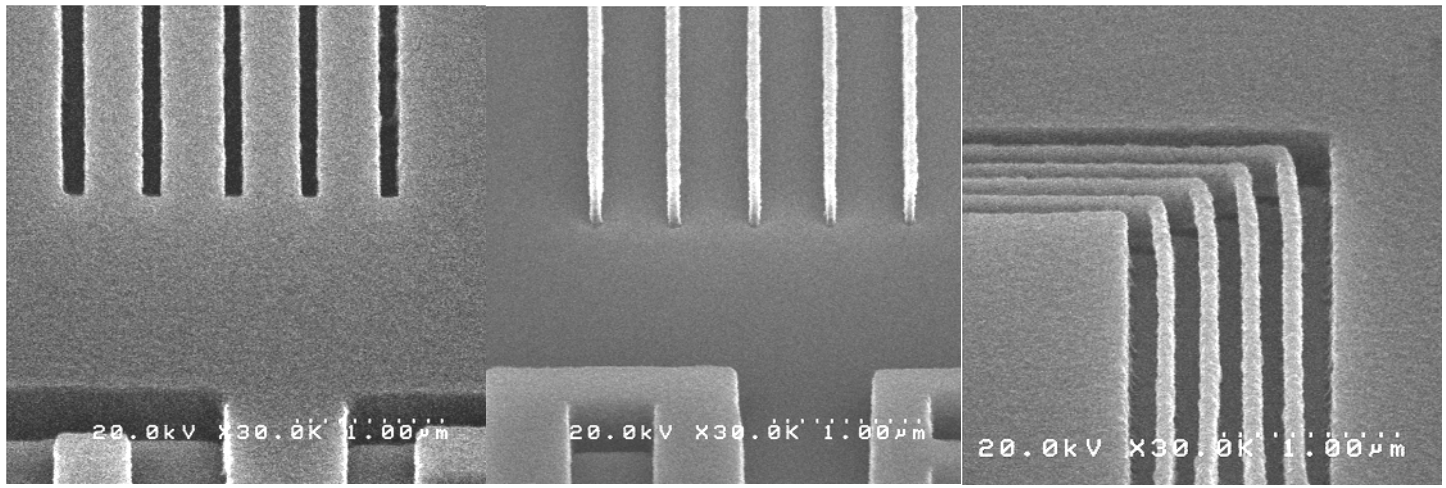


- Key assumptions:
  - Arrival statistics
    - chemistry
  - No other sources of blur
- CA materials PAG = 5%
  - PAG "scavenges" electrons
- Blur from aerial image, electron resist/substrate interactions, chemistry

$$\sigma_{total} = \sqrt{\sigma^2_{image} + \sigma^2_{chemistry} + \sigma^2_{scattering} + \sigma^2_{statistics}}$$

Advanced Resist Results

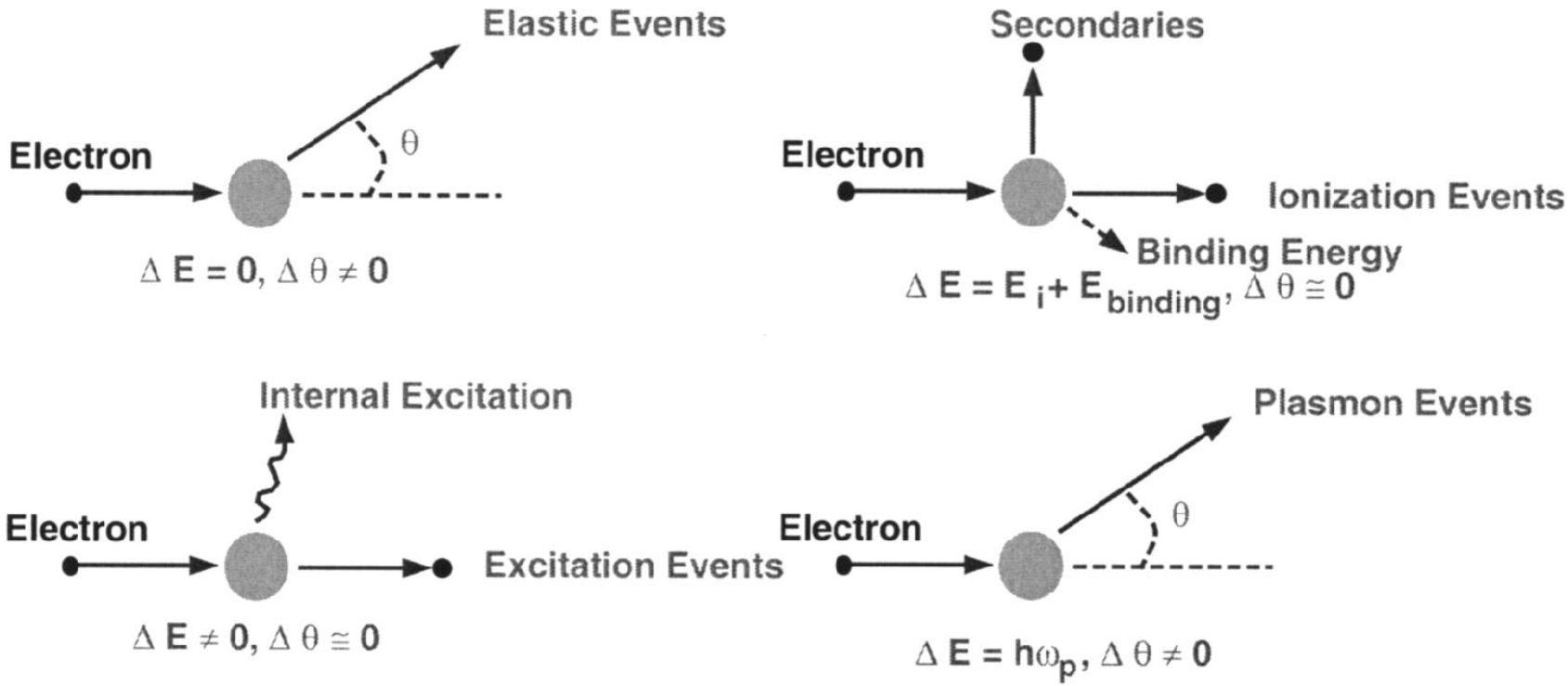
100 kV SCALPEL exposures



80 nm, 5.8 µC/cm^2 80 nm, 5.8 µC/cm^2 100 nm, 5.4 µC/cm^2

5.4 µC/cm^2 @ 100 nm feature size = 3375 electrons/100 nm pixel, $\sqrt{N}/N$ = 1.72%

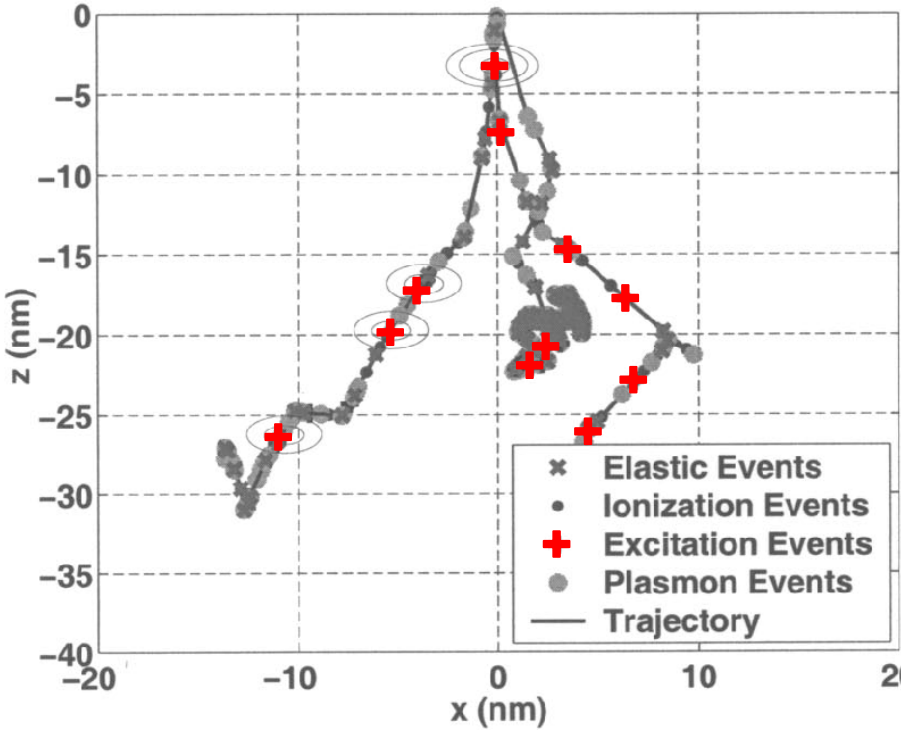
Energy Deposition I



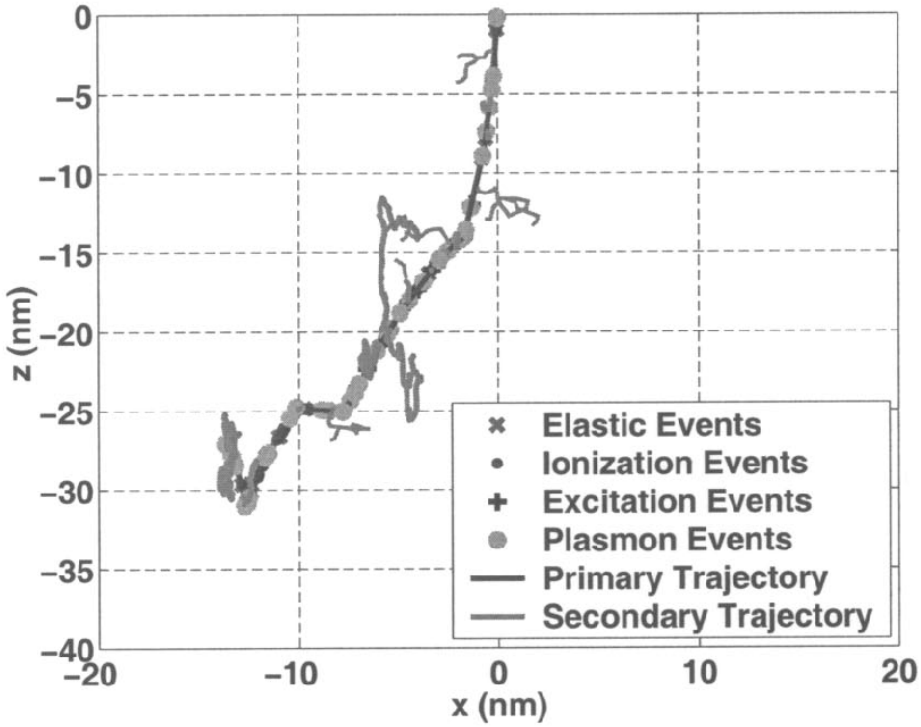
- Of the four different kinds of scattering events only two - excitation & ionization - result in chemical changes

"Comprehensive model of electron energy deposition", G. Han, M. Khan, Y. Fang, and F. Cerrina, *J. Vac. Sci. Technol.*, **B20** p2666 (2002)

Energy Deposition II



Trajectories of 3 primary 1keV electrons



Trajectories of 1 primary 1keV electrons and associated secondary electrons

- Excitation events are low energy and thus have large cross-sections, i.e. are substantially delocalized
- Secondary electrons also result in a substantial broadening of deposited energy profile

"Comprehensive model of electron energy deposition", G. Han, M. Khan, Y. Fang, and F. Cerrina, *J. Vac. Sci. Technol.*, **B20** p2666 (2002)

Energy Deposition vs Acid Generation in CA Materials

- Energy absorption process produces an ionized molecule, typically from the base resin
  - $RH \xrightarrow{h\nu} RH_{\bullet}^{+} + e^{-}, \quad RH_{\bullet}^{+} + e^{-} \longrightarrow RH^{*}$
  - In a non-polar material, electrons can recombine with counter-cation
- Electrons that escape recombination eventually thermalize
- Polar acid generator molecules effectively "scavenge" electrons
  - ➢ Ionization probability for acid generator is, to some extent, decoupled from fraction of PAG molecules
  - ➢ Acid formation occurs some distance (several nm) from site of energy absorption

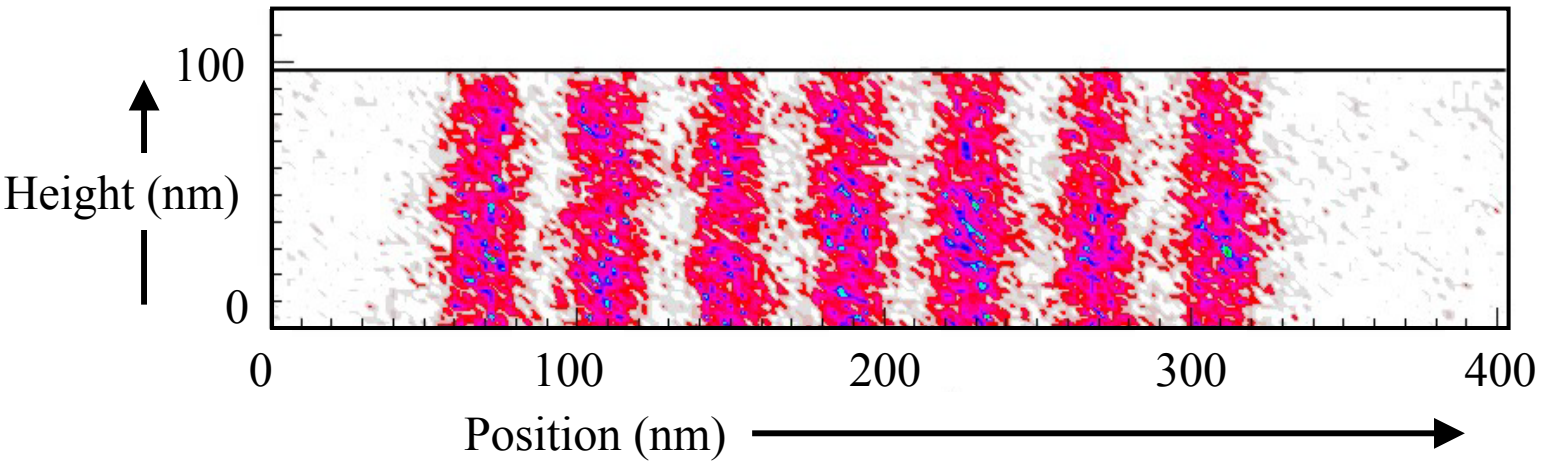
"Study on Radiation-Induced Reaction in Microscopic Region for Basic Understanding of Electron Beam Patterning in Lithographic Process I - Development of Subpicosecond Pulse Radiolysis and Relation Between Space Resolution and Radiation Induced Reaction of Onium Salt", T. Kozawa, A. Saeki, Y. Yoshida and S. Tagawa, *Jap. J. Appl. Phys.*, **41** p4208 (2002)

"Study on Radiation-Induced Reaction in Microscopic Region for Basic Understanding of Electron Beam Patterning in Lithographic Process II - Relation Between Resist Space Resolution and Space Distribution of Ionic Species", A. Saeki, T. Kozawa, Y. Yoshida and S. Tagawa, *Jap. J. Appl. Phys.*, **41** p4213 (2002)

Energy Deposition Distribution

- At high voltages (100 kV) and in thin (100 nm) resists, forward scattering is 5 – 10 nm (90% energy contour diameter) at the base of the film
- Exposure is accomplished by secondary electrons which peak in number at 10 eV
  - Mean free paths of a few nanometers

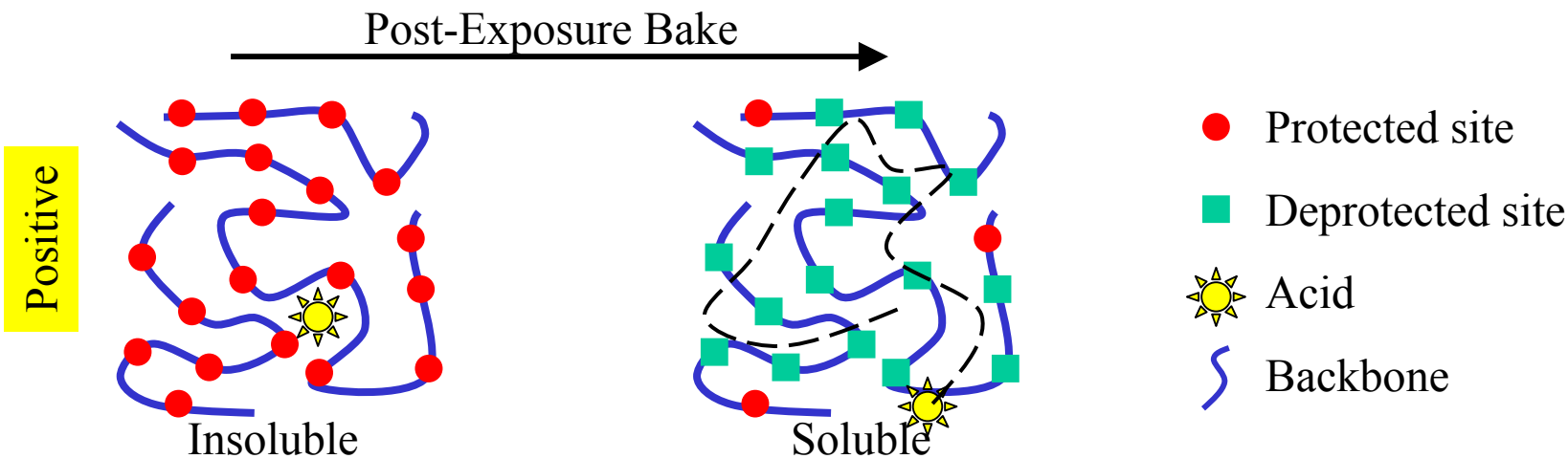
➢ Even with very finely focused beams resolution is limited by the nature of the electron solid interactions



Monte-Carlo simulation of the energy deposition distribution for 20 nm lines & spaces. δ-function incident beam assumed. 20 μC/cm^2 dose.

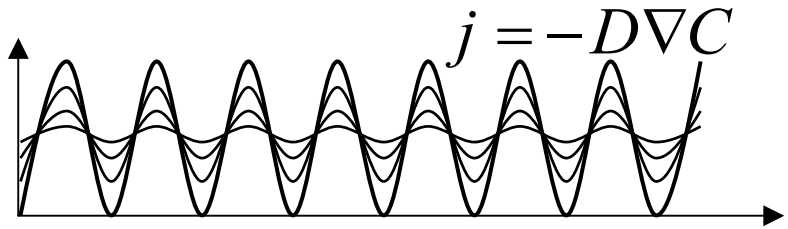
Chemically Amplified Resists - Diffusion I

- Acid diffusion in CA materials is highly complex:
  - Motion of H^+ affected by anion and by polar functionalities of resist
    - Diffusion coefficient changes with extent of deprotection reaction
    - Catalytic chain lengths can be > 1000
    - However, diffusion distances can be as small as 5 nm



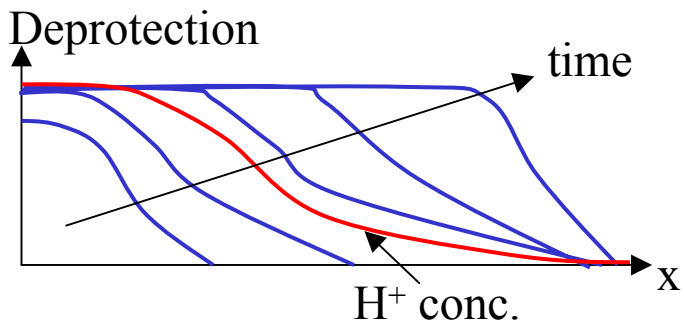
Chemically Amplified Resists - Diffusion II

- Acid concentration profile formed upon exposure - diffusion will homogenize distribution
- Reaction-diffusion model accounts for changing diffusion coefficients as deprotection reaction proceeds and material changes from non-polar to polar, for changing deprotection rates as concentration of protecting groups changes and for reduction of acid concentration through various loss mechanisms
  - Diffusion coefficients for TBI-PFBS at 105 °C in PTBOCST: **15 nm²/s** (protected), **0.1 nm²/s** (deprotected). Smaller PAG anions allow faster diffusion.
  - Deprotection reaction proceeds (slowly) even at low acid concentrations ⇒ blurring
  - Base added to films to reduce acid levels in nominally unexposed areas



$$\frac{\partial C}{\partial t} = -\nabla(D\nabla C)$$

Concentration dependent diffusion



"Chemical and Physical Aspects of the Post-Exposure Baking Process Used for Positive-Tone Chemically Amplified Resists", W.D. Hinsberg, F.A. Houle, M.I. Sanchez and G.M. Wallraff, *IBM J. Res. & Dev.*, **45** p667 (2001)

"Method of Measuring the Spatial Resolution of a Photoresist", J.A. Hoffnagle, W.D. Hinsberg, M.I. Sanchez and F.A. Houle, *Optics Letters*, **27** p1778 (2002)

Statistics of Resist Roughness

Process Flow ⇒ Multiple Statistics

- Dose Statistics: Probability distribution for # of electrons/"pixel".
- Acid Release Statistics: Probability of Acid Release given presence of an electron.
- PEB Statistics: Probability of deprotection given Acid Random Walk
- Dissolution Rate Statistics: Concatenate above statistics
  Deprotection/Acid Density,
  Dissolution Rate/Deprotection Density…
- Surface Statistics: Compute Surface Evolution using Rate Statistics

Assume Positive Chemically Amplified Resist
Straightforward modification for negative resist

"Analytical Model of the 'Shot Noise' Effect in Photoresist", G.M. Gallatin and J.A. Liddle, *Microelectronic Engineering,* **46** p365 (1999)
"Continuum Model of Shot Noise and Line Edge Roughness", G.M. Gallatin, *Proc. SPIE*, **4404** p123 (2001)

Line Edge Roughness

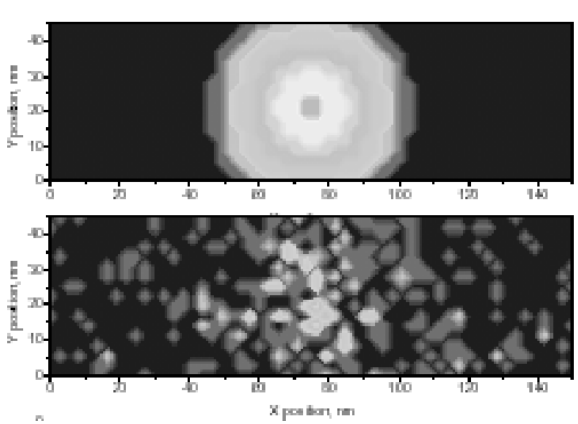
- Roughness depends directly on dissolution rate
  - Exposure ⊗ Latent Image ⊗ PEB statistics washes out effect of shot-noise
- LER increases with decreasing image edge slope
- Minimum value of roughness is related directly to granularity of resist
  - In conventional materials, the size of a molecule
  - In CA materials, the molecular size or the volume deprotected by an acid molecule during PEB (links resolution and sensitivity)

LER Simulation

48 nm contact

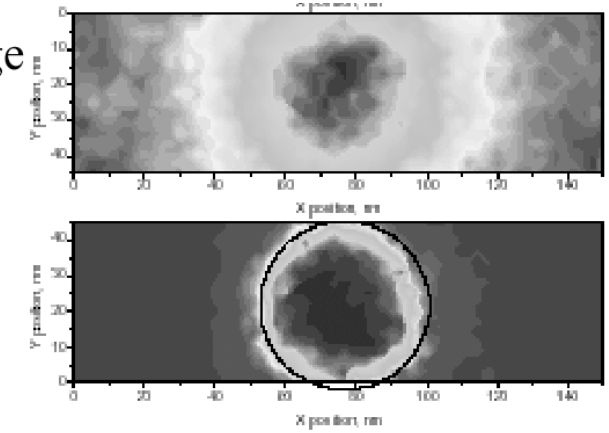
Intial acid image

Acid after PEB

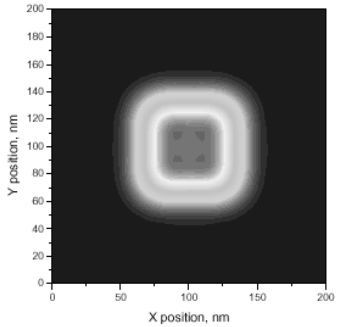


Resist image after PEB

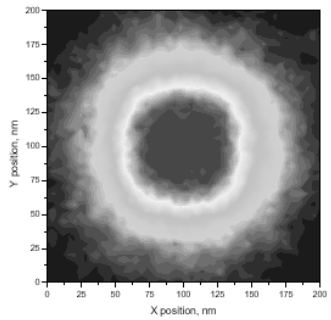
Developed contact



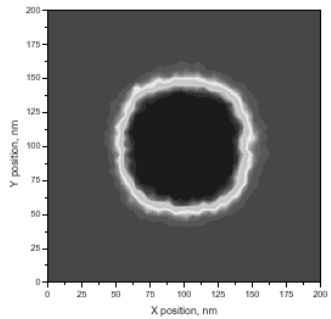
Photons



Deprotected Polymer



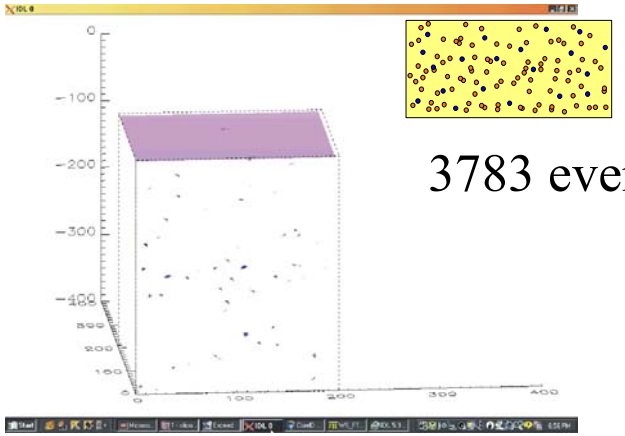
Dissolved Polymer



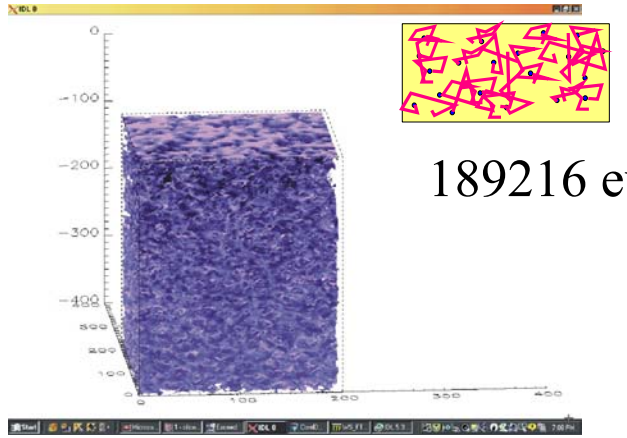
- Influence of different stages of image formation process in a chemically amplified resist on the final, developed feature

"The Estimated Impact of Shot Noise in Extreme Ultraviolet Lithography", J. Cobb, F. Houle and G. Gallatin, to appear in *Proc. SPIE*, Microlithography Conference (2003)

Step-by-step Image Formation in EP-004 at 3 μC/cm^2

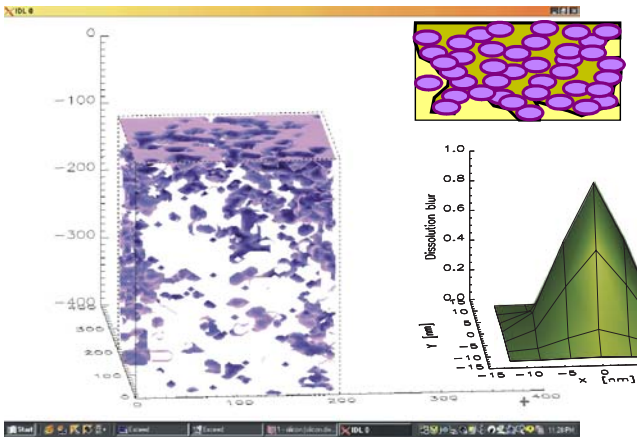


3783 events

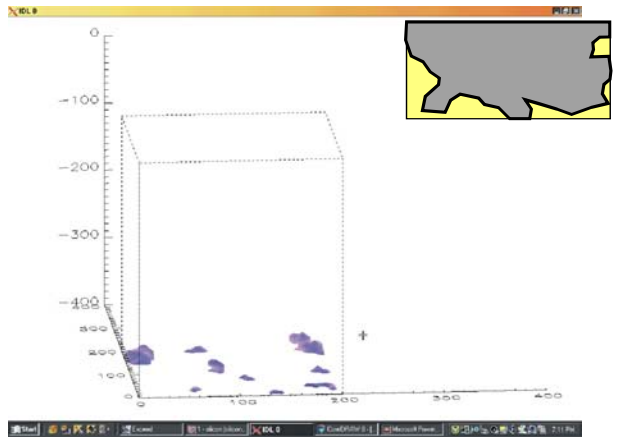


189216 events

- Photoacid events
- Amplification events



3-D convolution function

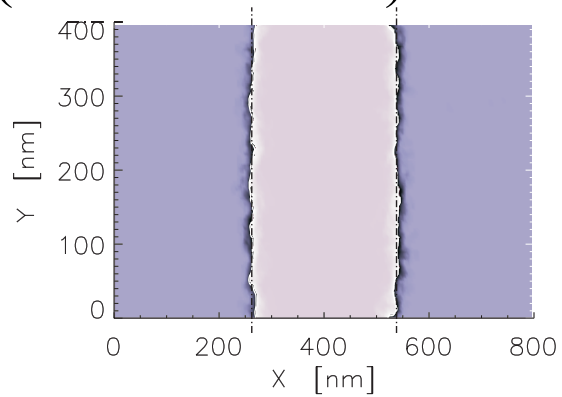


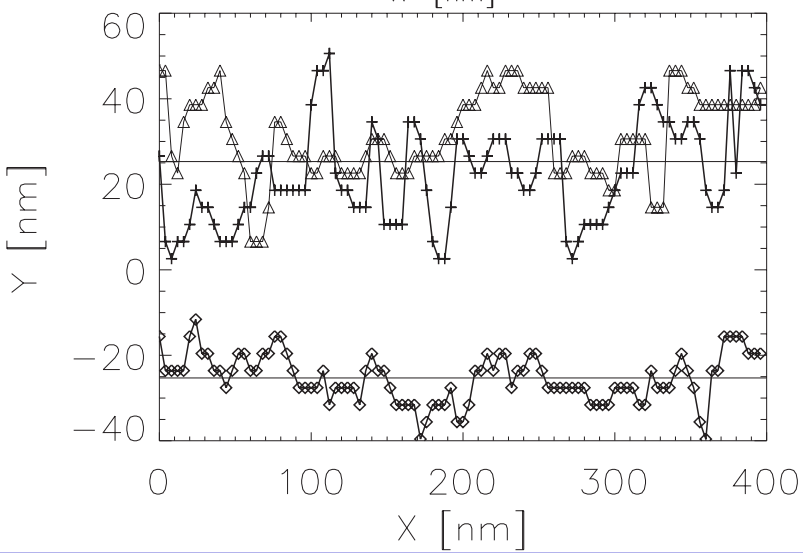
- Solubility change
- Development

"Reist Requirements for Electron Projection and Direct Write Nanolithography", L.E. Ocola, Mat. Res. Soc. Symp. Proc., **705** Y1.1.2 (2002)

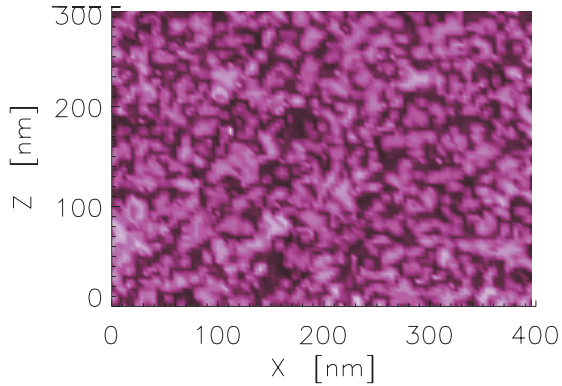
Simulated SEM & AFM LER of a Resist Feature

- Simulated SEM image (50% threshold)





- Simulated AFM sidewall image



- AFM LER (1σ):
  - Simulated: 10.7 nm
  - Experiment: NA
- SEM LER (1σ):
  - Simulated: 5.7 nm
  - *Experiment: 3 nm*

L.E. Ocola

Performance Limits

- Resolution and sensitivity are strongly coupled
- Resolution is determined by

$$\sigma_{total} = \sqrt{\sigma^2_{image} + \sigma^2_{chemistry} + \sigma^2_{scattering} + \sigma^2_{statistics}}$$

- Image blur can be reduced to 0.5 nm
- Statistical blur can be reduced by going to high doses
- Chemical blur can be reduced by using non-CA materials or curtailing acid diffusion
- Scattering blur can only be reduced by changing the nature of the electron solid interactions
  - High energy processes are localized to the incident beam
    - Hole drilling in inorganic resists
    - Radiation damage in $Si0_2$

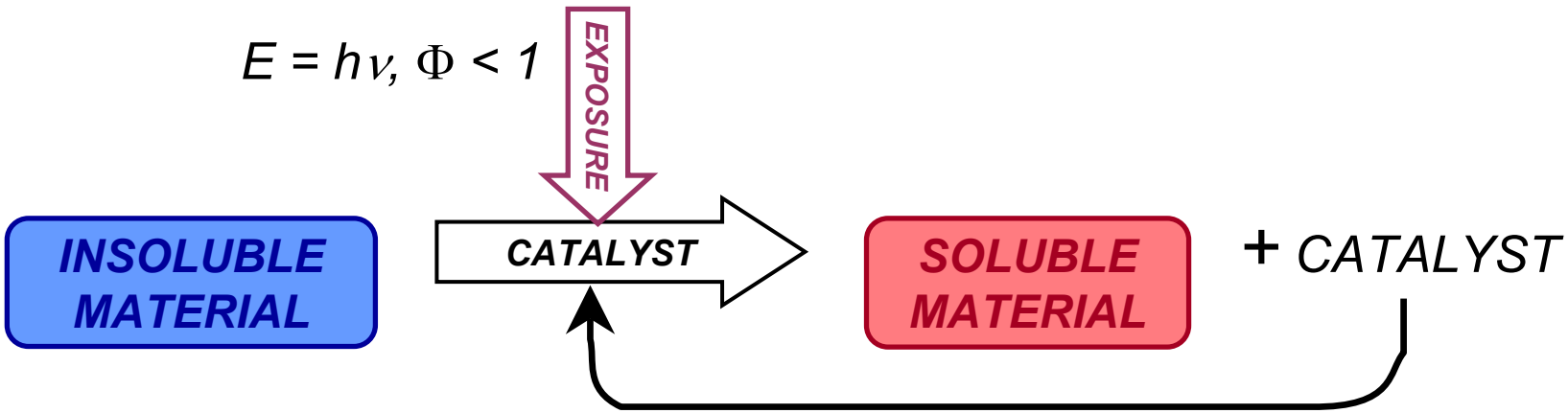
"Resist Requirements and Limitations for Nanoscale Electron Beam Patterning", J.A. Liddle, G.M. Gallatin and L.E. Ocola, Mat. Res. Soc. Symp. Proc. (2002)
"Resolution Limits for Electron-Beam Lithography", A.N. Broers, *IBM J. Res. Develop.*, **32** p502 (1988)

Resolution limitations in chemically amplified photoresist systems

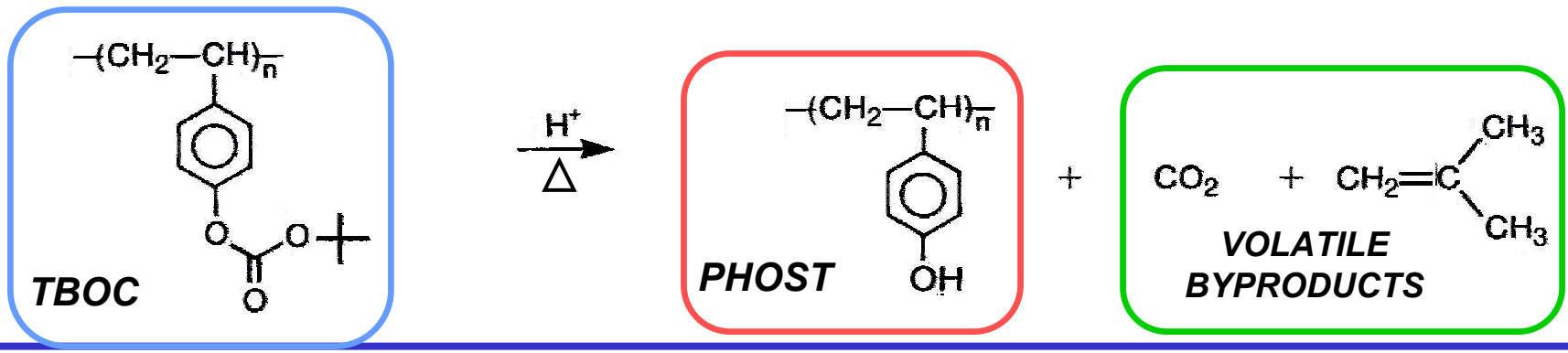
Chemical amplification

Hundreds of solubility conversion reactions per absorbed photon.

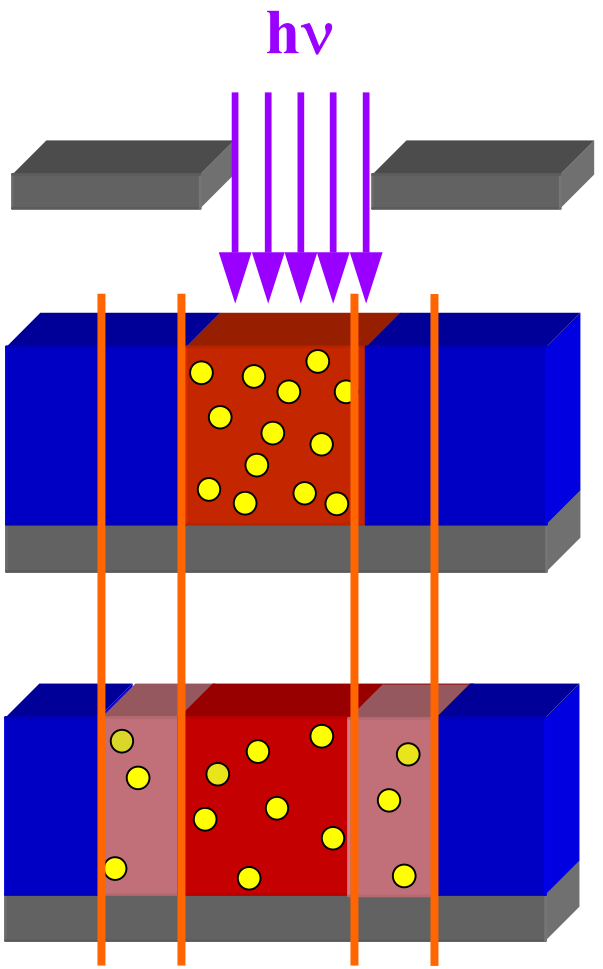
General positive-tone function:



Model system:



Intrinsic limitation?



Exposure

Generation of chemically stable catalyst

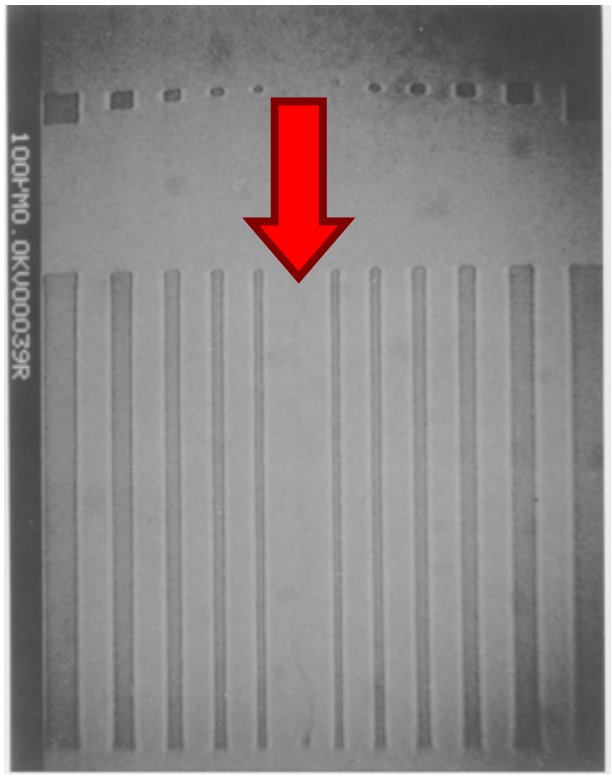
PEB

Solubility-switching plus transport

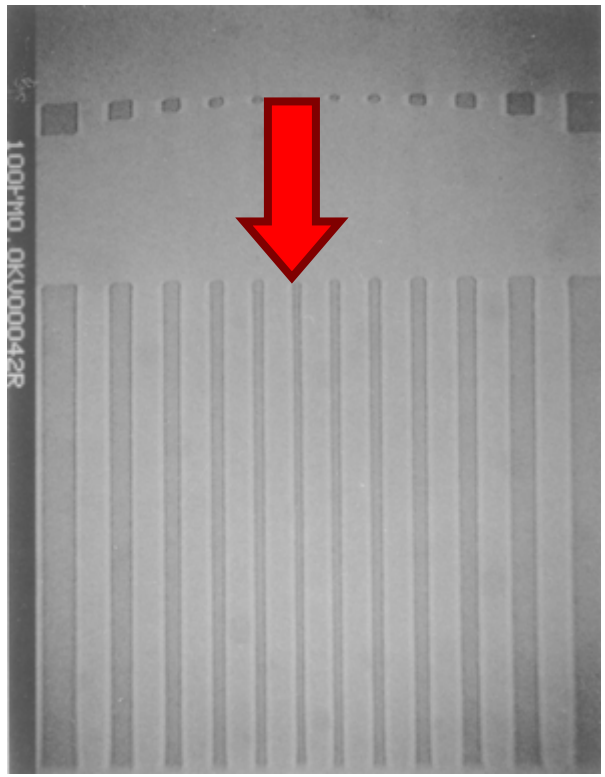
Diffusion Bias

Previous work: FIB exposure

STEM exposure of TBOC photoresist on thin silicon nitride membranes.



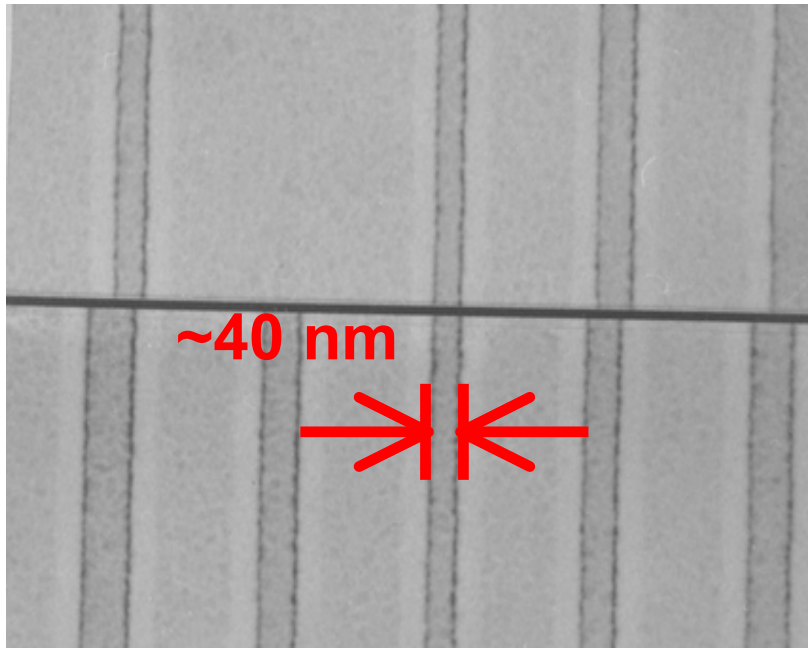
Lower dose
Smallest feature not resolved



Higher dose
Smallest feature resolved

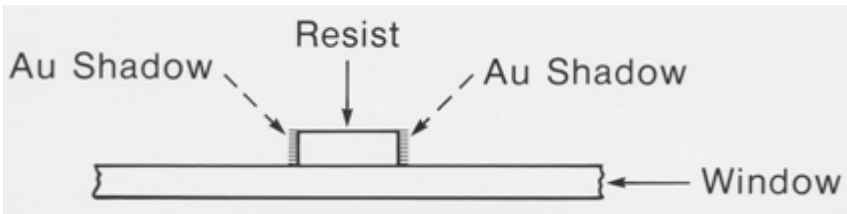
C. P. Umbach, A. N. Broers, C. G. Willson, R. Koch, and R. B. Laibowitz,
J. Vac. Sci. Technol. B 1988,6, 319-322

Previous work: FIB exposure



TBOC resolution:

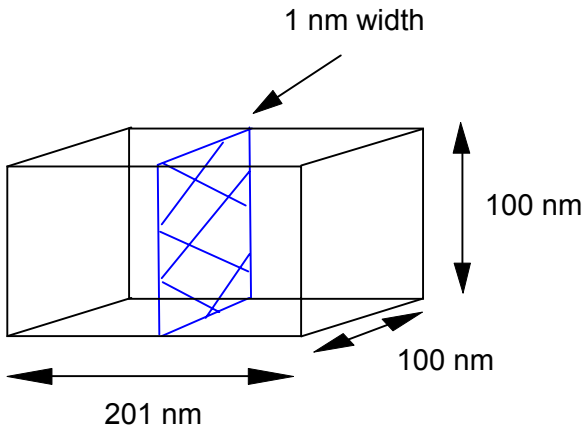
~40 nm in 1988



➔ ***Minimum resolved feature size is ~40 nm***

Line spread function calculation

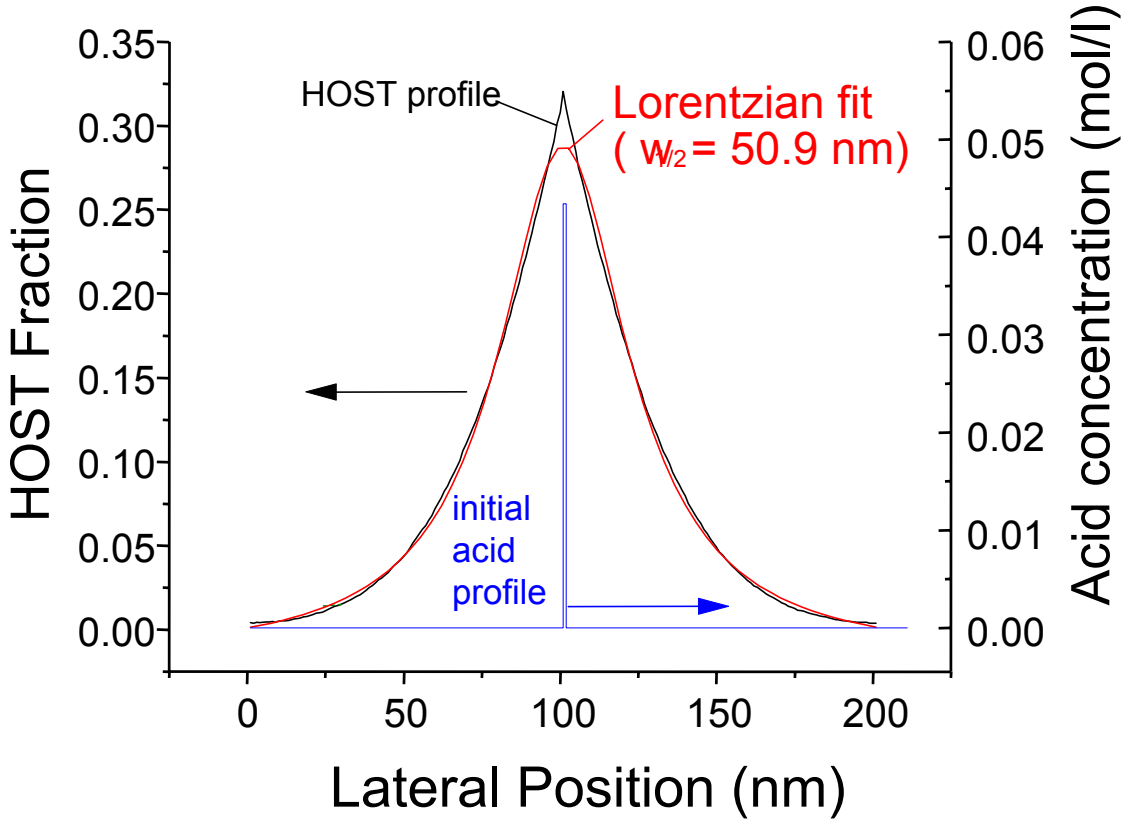
W. Hinsberg, F. Houle, M. I. Sanchez, J. Hoffnagle, G. Wallraff, D. R. Medeiros, G. Gallatin, and H. Cobb, Proc. SPIE, ***2003****.*



Calculated using quantitative physically-based, experimentally validated PEB model.

PEB 120 sec, 100 °C

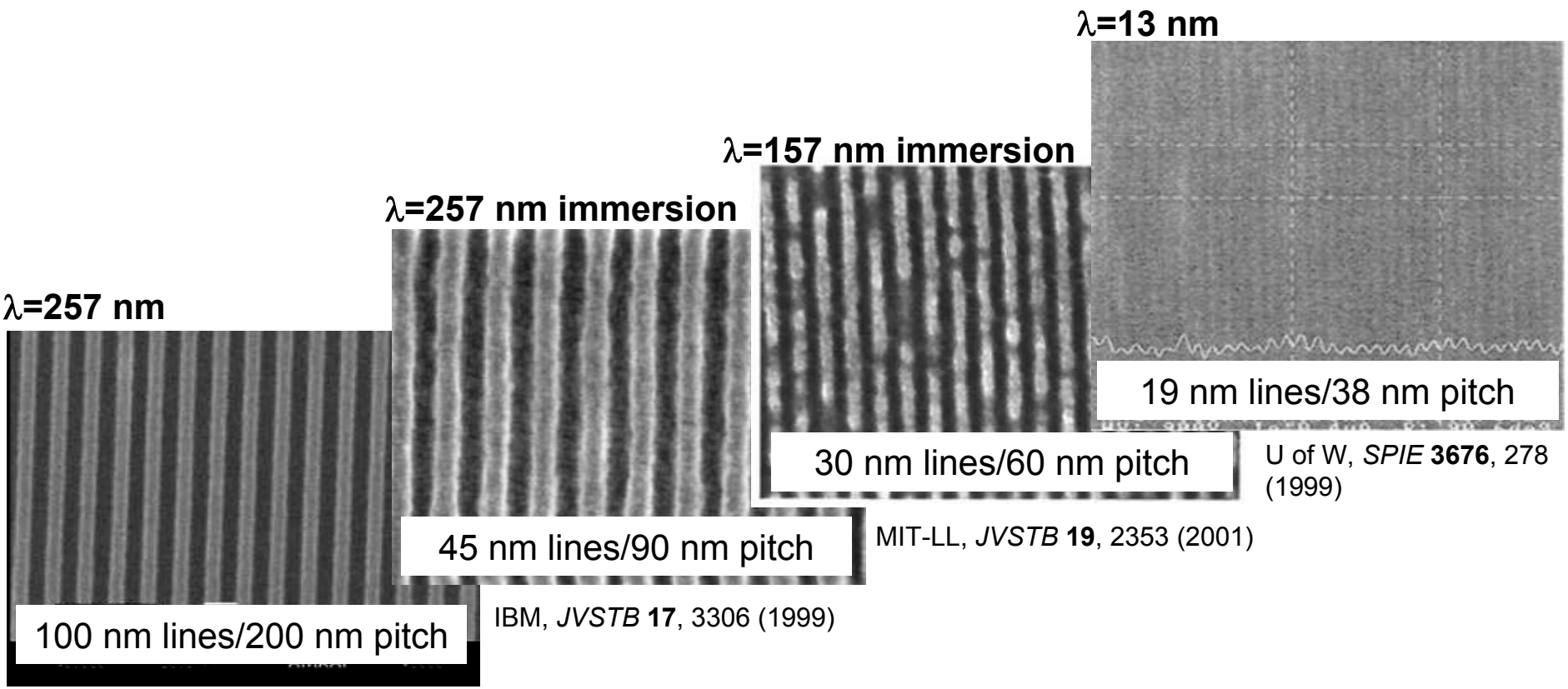
PTBOCST/TBI-PFBS



➔ ***Predicted feature size is <~50 nm***

Interferometric lithography of ESCAP chemically amplified resists

*W. Hinsberg, F. Houle, M. I. Sanchez, J. Hoffnagle, G. Wallraff, D. R. Medeiros, G. Gallatin, and H. Cobb, Proc. SPIE, **2003**.*



U of W, *SPIE* **3676**, 278 (1999)

MIT-LL, *JVSTB* **19**, 2353 (2001)

IBM, *JVSTB* **17**, 3306 (1999)

➔ ***Minimum resolved feature size is ~ 30 - 45 nm***

Routes to reduced diffusion bias

- ***Use lower PEB temperature***

  Reduces diffusion rate, also reduces reaction rate

- ***Add base to formulation to quench diffusing acid***

  "Scavenges" diffusing acid, also scavenges other acid

- ***Increase size of diffusing acid species***

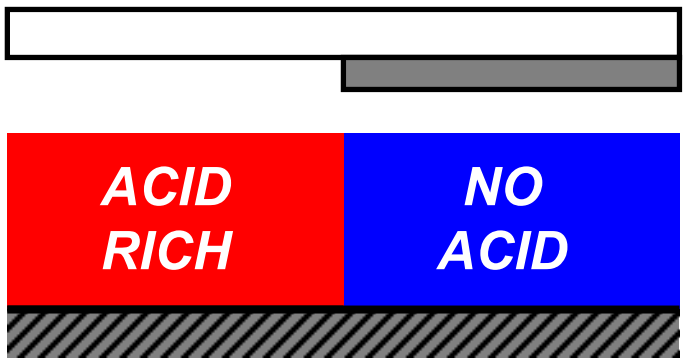
  Reduces diffusion rate, can also limit catalytic efficiency

Diffusion bias measurements

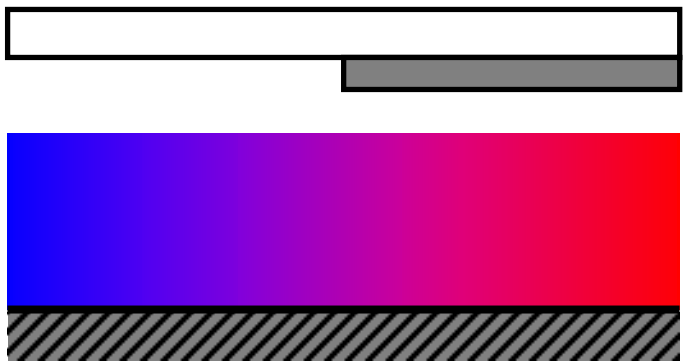
Goal is to measure change in acid distribution due to diffusion

→ *Best to start with a well-defined acid distribution*

IDEAL ACID DISTRIBUTION



ACTUAL ACID DISTRIBUTION

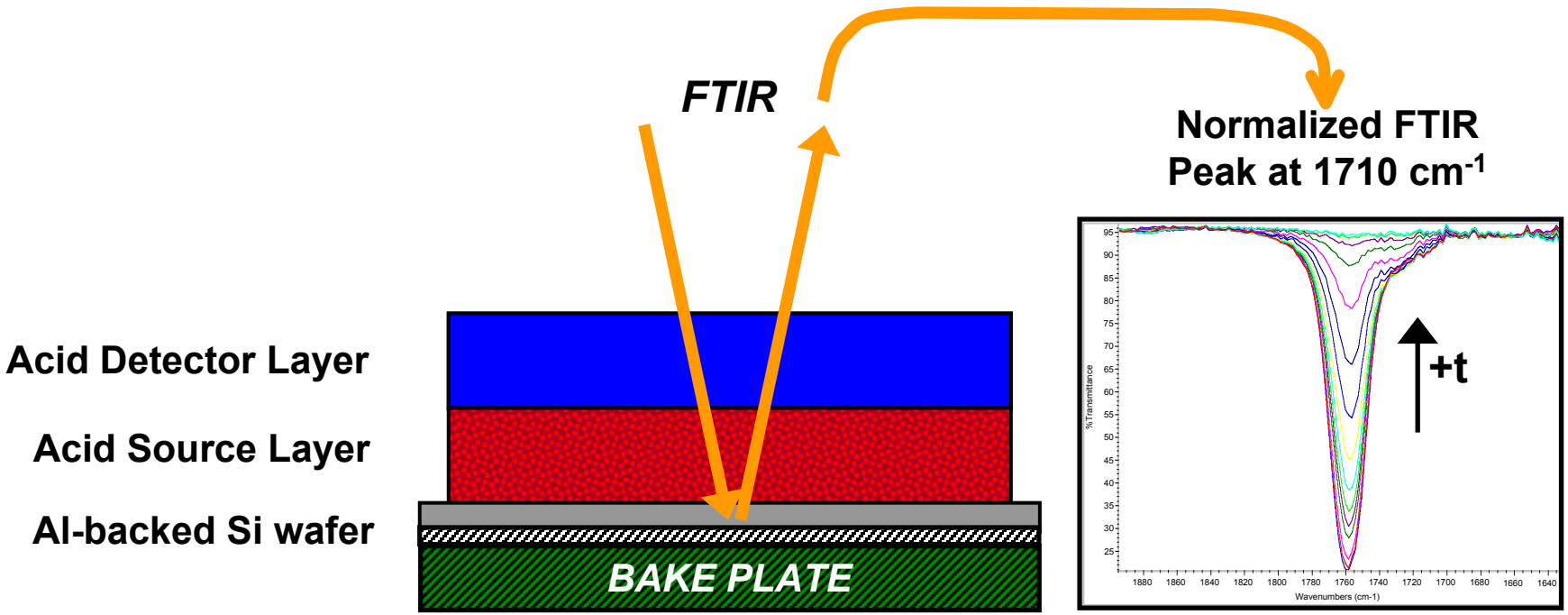


Our approach: Bilayer systems

BILAYER ACID DISTRIBUTION

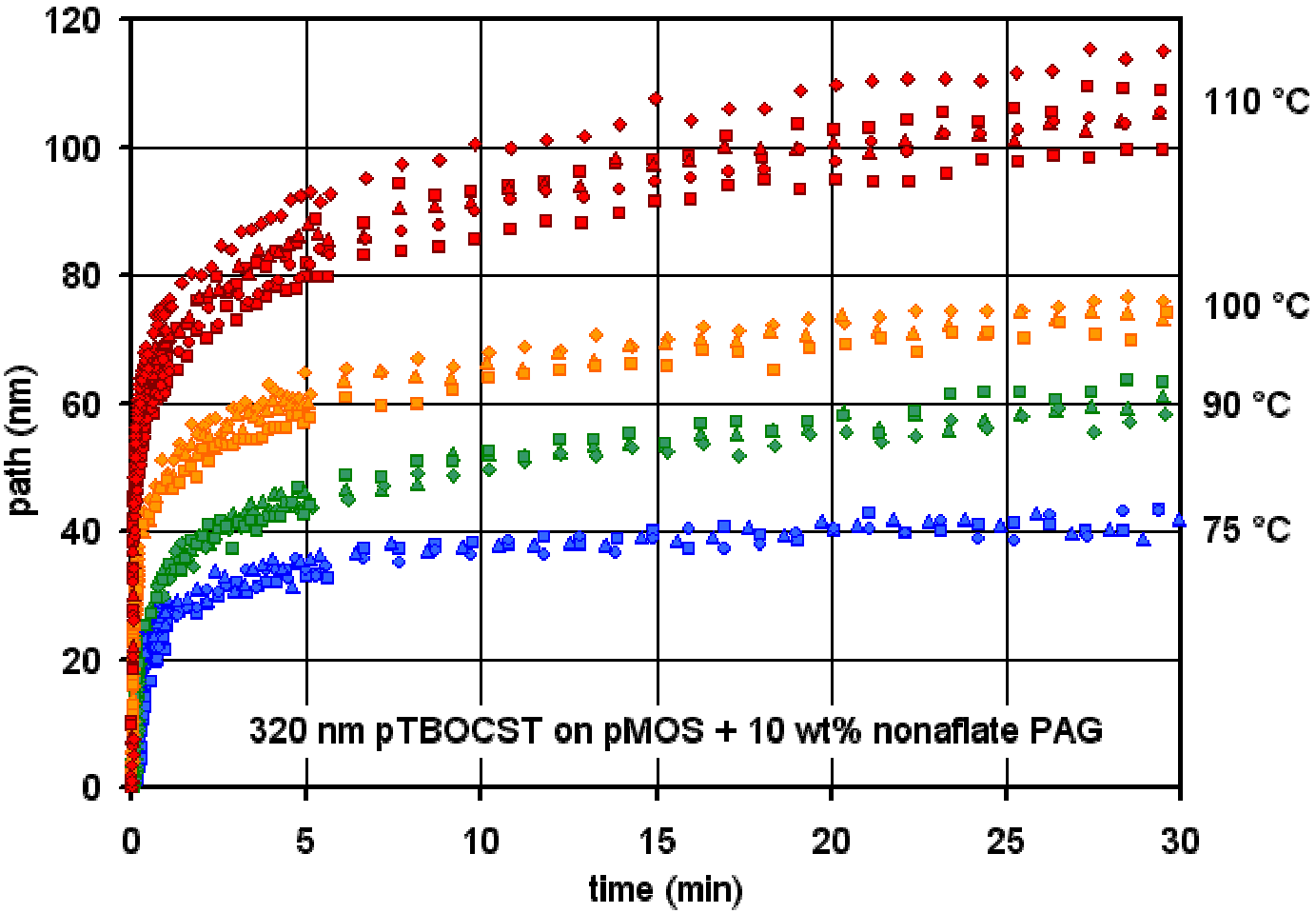
FTIR measurements

Measure acid diffusion distance by monitoring the reaction of acid with TBOC polymer.



Effect of PEB temperature

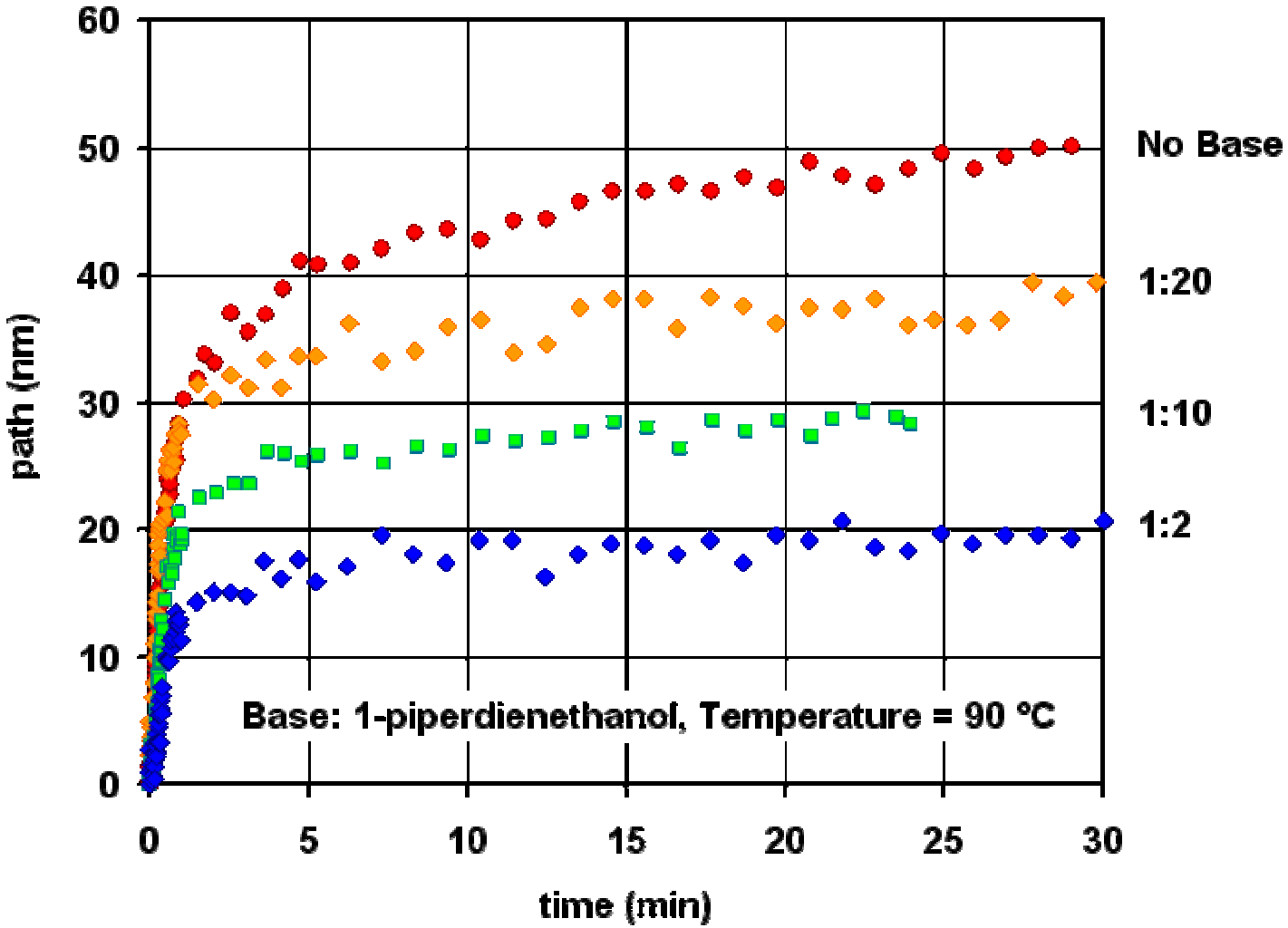
→ ***Reduce PEB temperature, reduce bias***



→ ***Smallest measured diffusion bias is ~25 nm***

Effect of added base

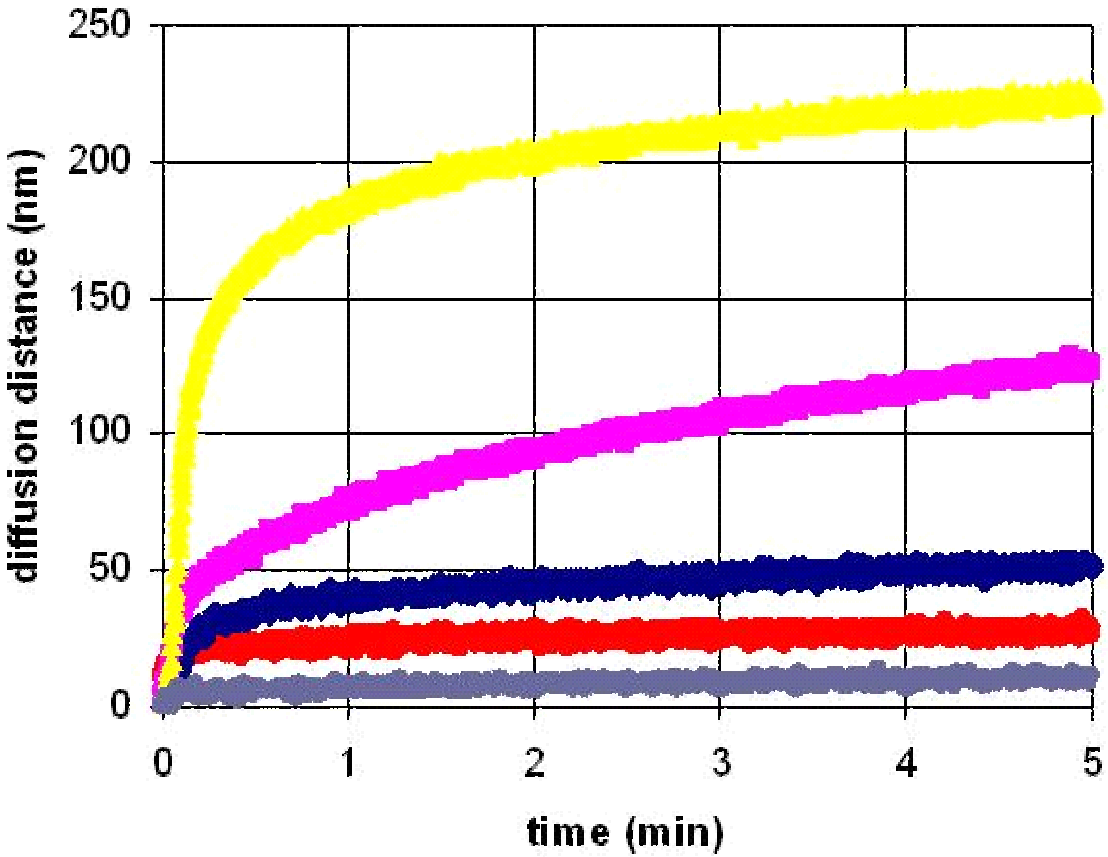
→ ***Increase base loading, decrease bias***



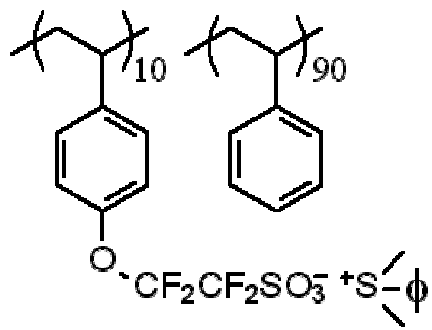
→ ***Smallest measured diffusion bias is ~15 nm***

Effect of size of diffusing species

→ ***Increase the size of the acid anion, reduce diffusion***



Polymeric PAG



→ ***Smallest measured diffusion bias is ~15 nm***

Neutron Reflectivity

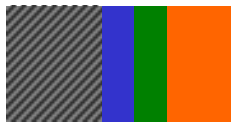
➔ ***Neutron reflectivity is sensitive to deuterium concentration with nanometer resolution.***

1) Spincoated d-tBOC film

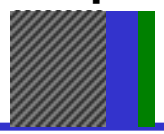
2) Coat PHS+PAG layer

3) UV Exposure

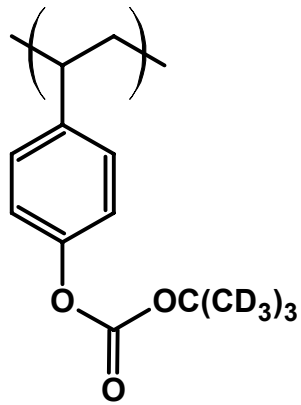
4) Bake film stack



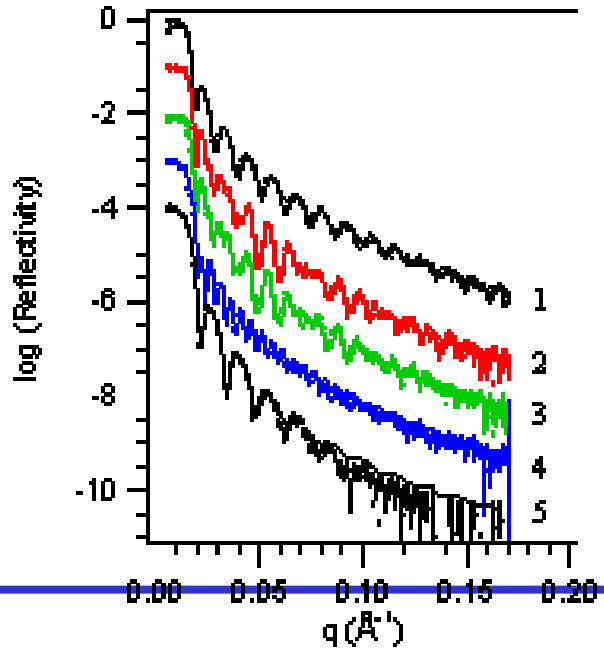
5) Develop



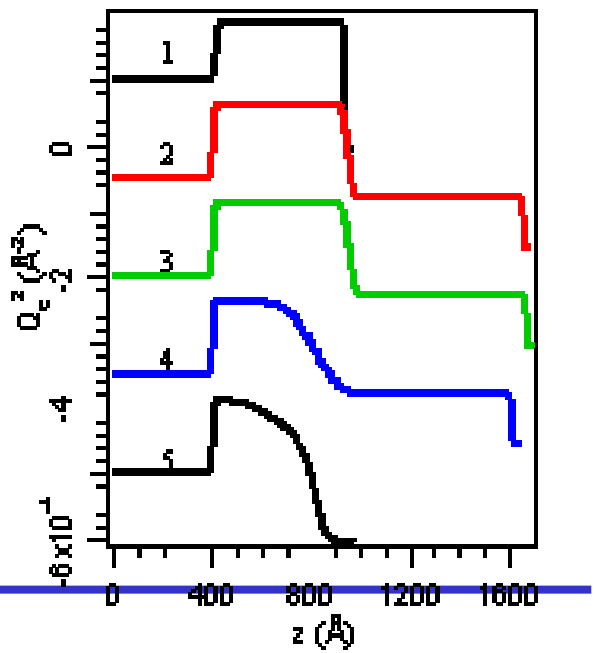
Structure of deuterated t-BOC:
- Deuterium-containing group is removed by the deprotection reaction



Raw data and fit



Real space profiles

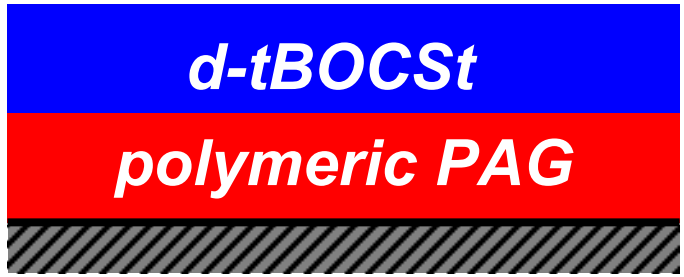


(Lin *et al.*, Science, 2002)

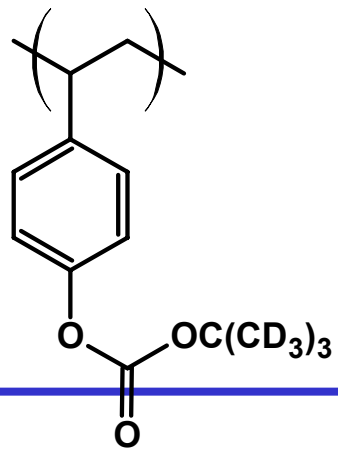
Effect of size of diffusing species

Neutron reflectivity measurements

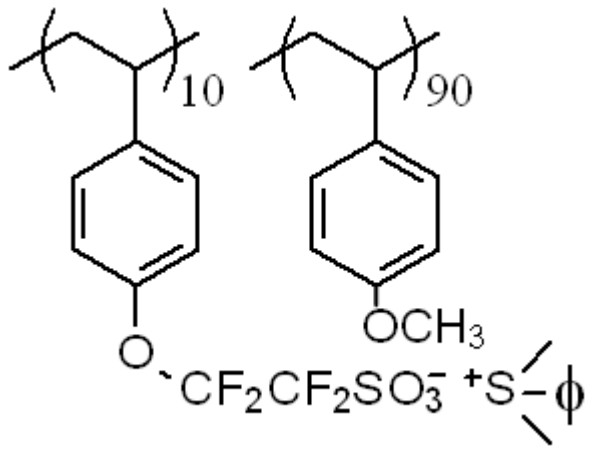
Bilayer film stack with neutron contrast:



Structure of deuterated t-BOCSt:
- Deuterium-containing group is removed by the deprotection reaction

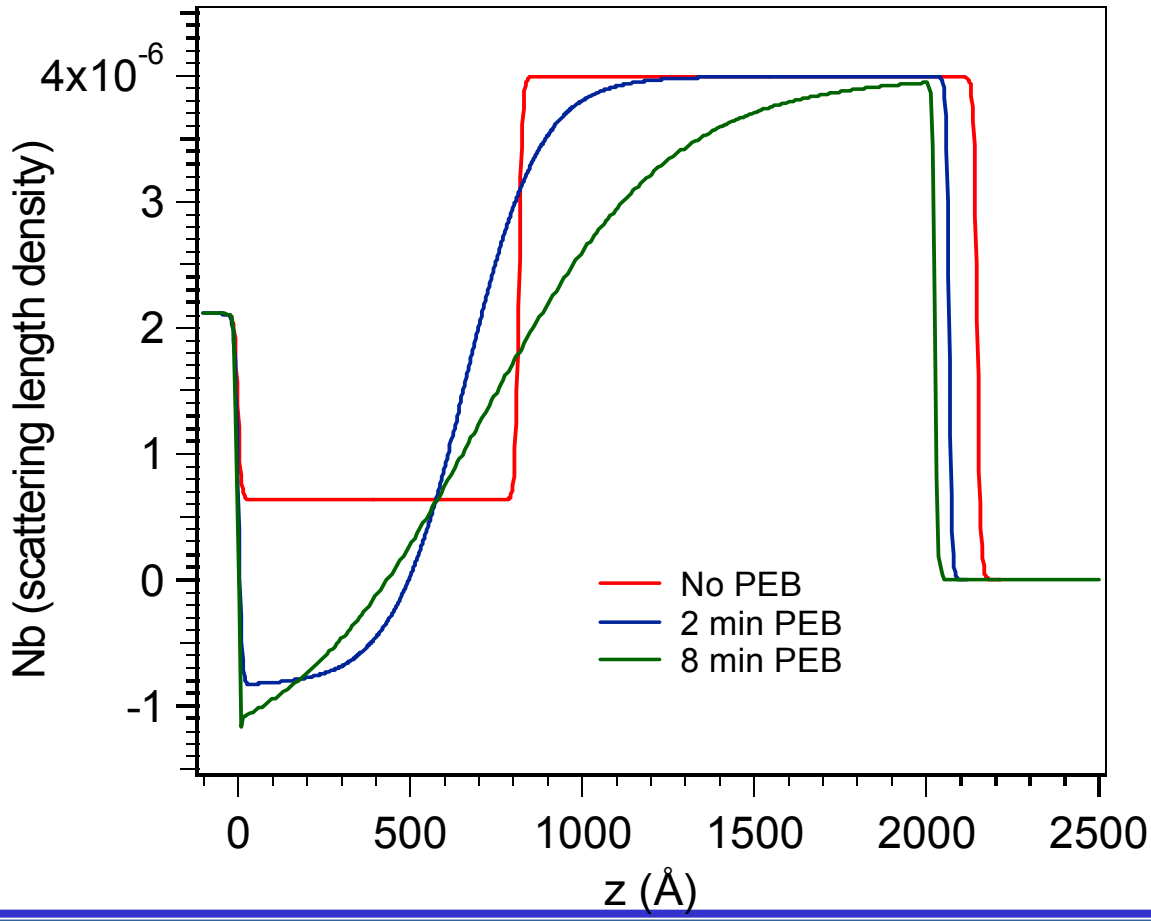


Structure of polymeric PAG:
- Produces a bound acid molecule



Neutron reflectivity measurements

After a 2 min bake at 90 °C, interfacial width is ~ 19 nm between polymeric PAG layer and TBOC layer.



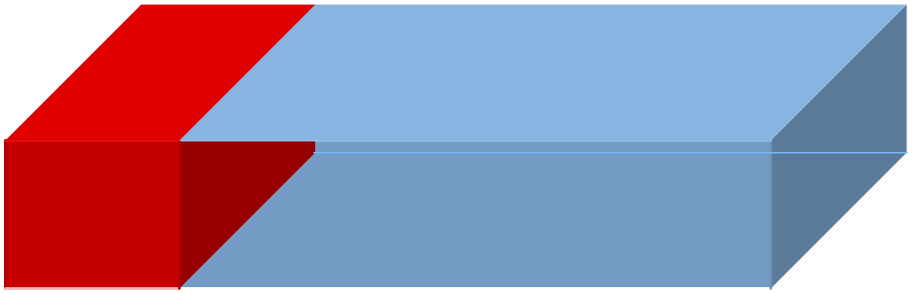
➔ ***Smallest measured diffusion bias is ~ 19 nm***

Conclusions

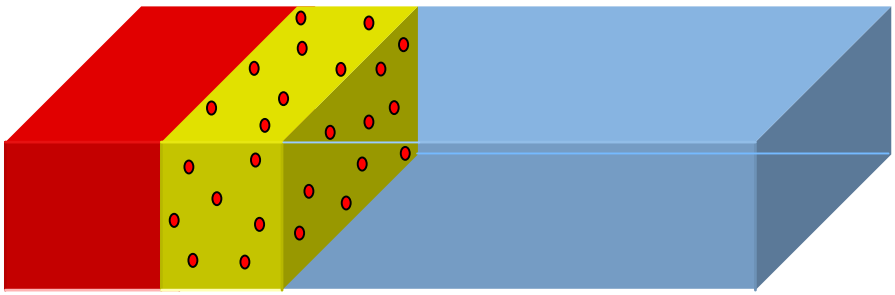
There is an apparent resolution limit to chemically amplified photoresist systems in the range of ~30-40 nm (minimum diffusion bias of ~15-20 nm).

It appears that the mechanisms responsible for high sensitivity in these resists are intrinsically tied to the processes that result in diffusion-induced bias.

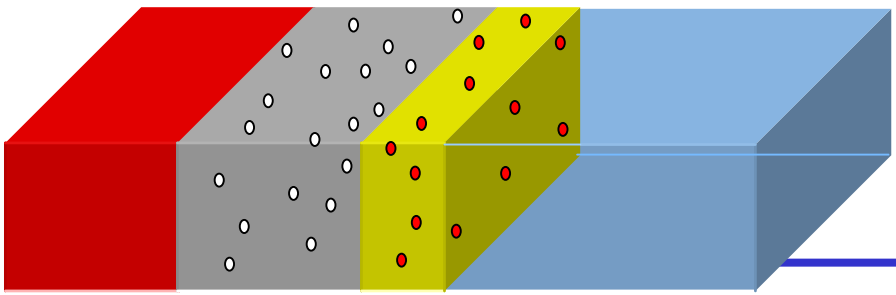
Image blur: Reaction Front



Initial Condition



Reaction Front Formation



Gradual Depletion of Front

High acid concentration region

Reaction zone

Reacted region (Bias region)

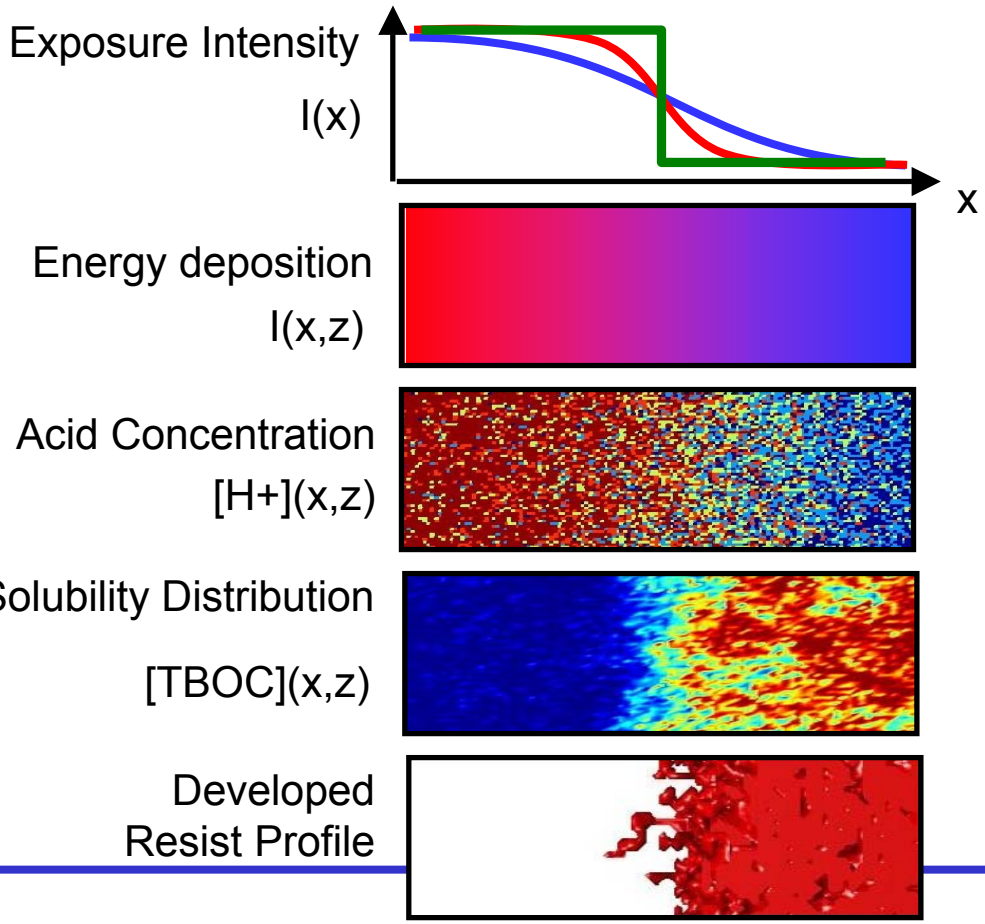
Unreacted region

- Active (mobile) acid molecules

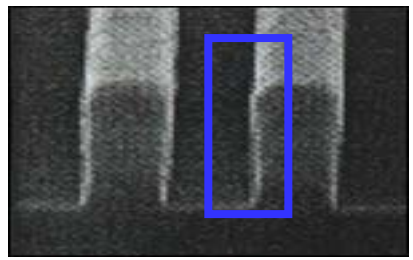
- Inactive (immobile) acid molecules

Origins of Resist Feature Roughness

Mesoscale simulations can be used to study the formulation variables and processing conditions that contribute to photoresist roughness.

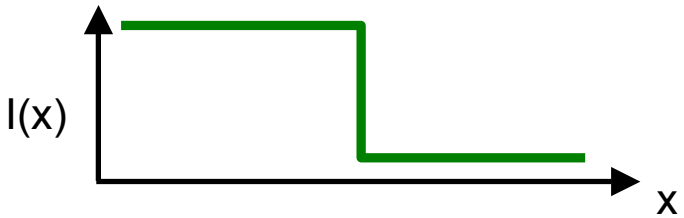


Simulation Region



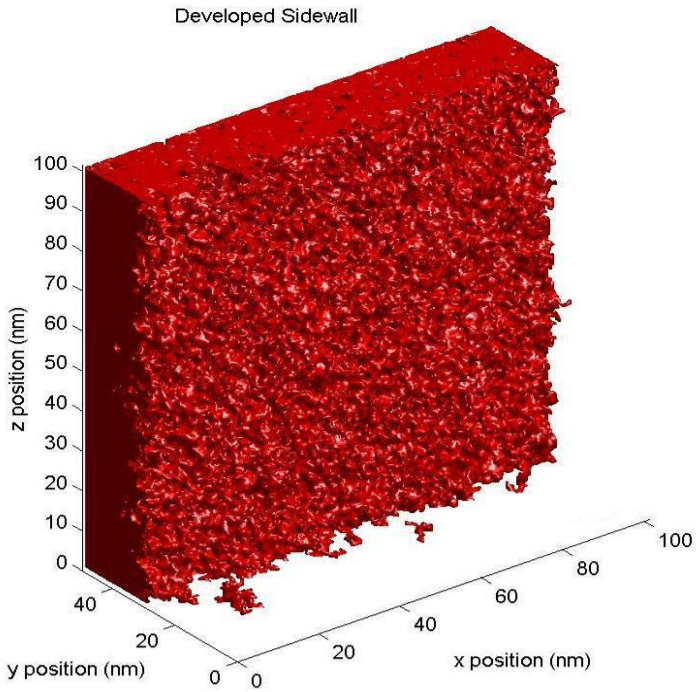
Origins of Resist Feature Roughness

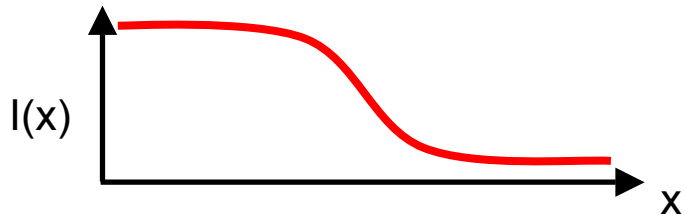
For poor exposure contrast, spatial irregularities exist over a larger portion of the line edge, resulting in greater feature roughness.



Step Function Exposure

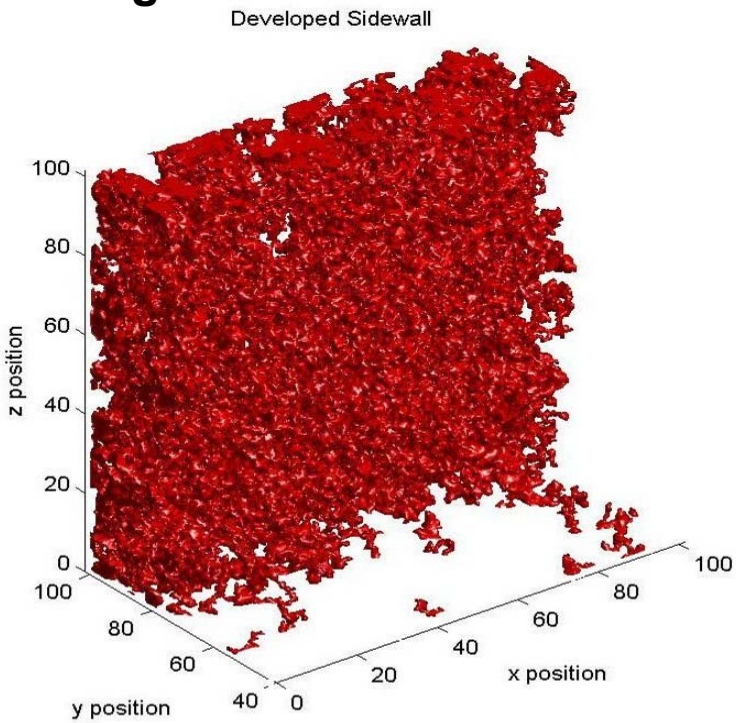
Roughness = 2.58 nm RMS





Low Contrast Exposure

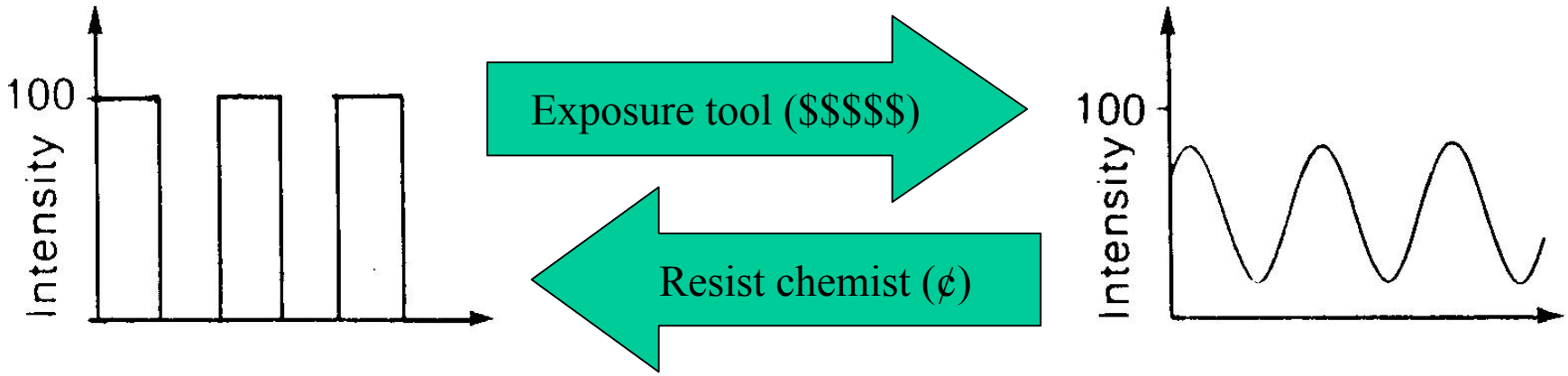
Roughness = 10.74 nm RMS



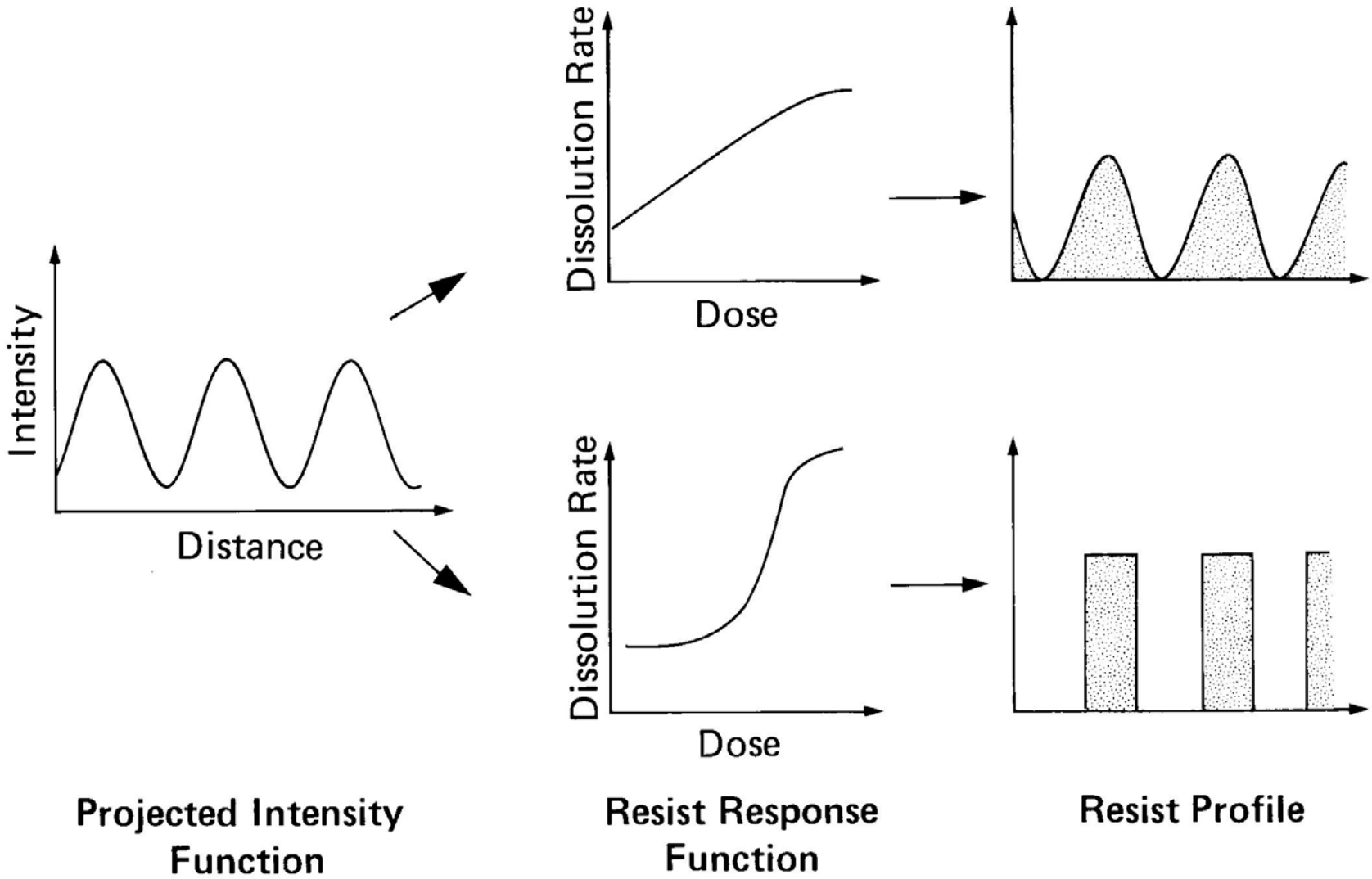
Gerard: Design of Resist Materials

- Imaging mechanisms
  - "Traditional"
    - Chain scission – positive tone, CA unzipping
    - Cross-linking – negative tone
    - Polarity switch – usually positive tone
  - Non-traditional
    - Top surface imaging, silylation, graft polymerization
- "Photo-" (for photoresists, different for e-beam resists)
  - Photochemistry, bleaching
  - Optical properties, absorbance
- "-Resist"
  - Dry etch resistance, Onishi parameter, hard masks
- Mechanical stability
  - Swelling, aspect ratio – CARC
- Environmental stability, shelf life, outgassing, contamination
- Process window, pre- and post-exposure delay stability
- Manufacturability of resist
  - Copolymerization vs. additives

Importance of resist contrast



Importance of resist contrast



Resist contrast mechanisms

Liquid development

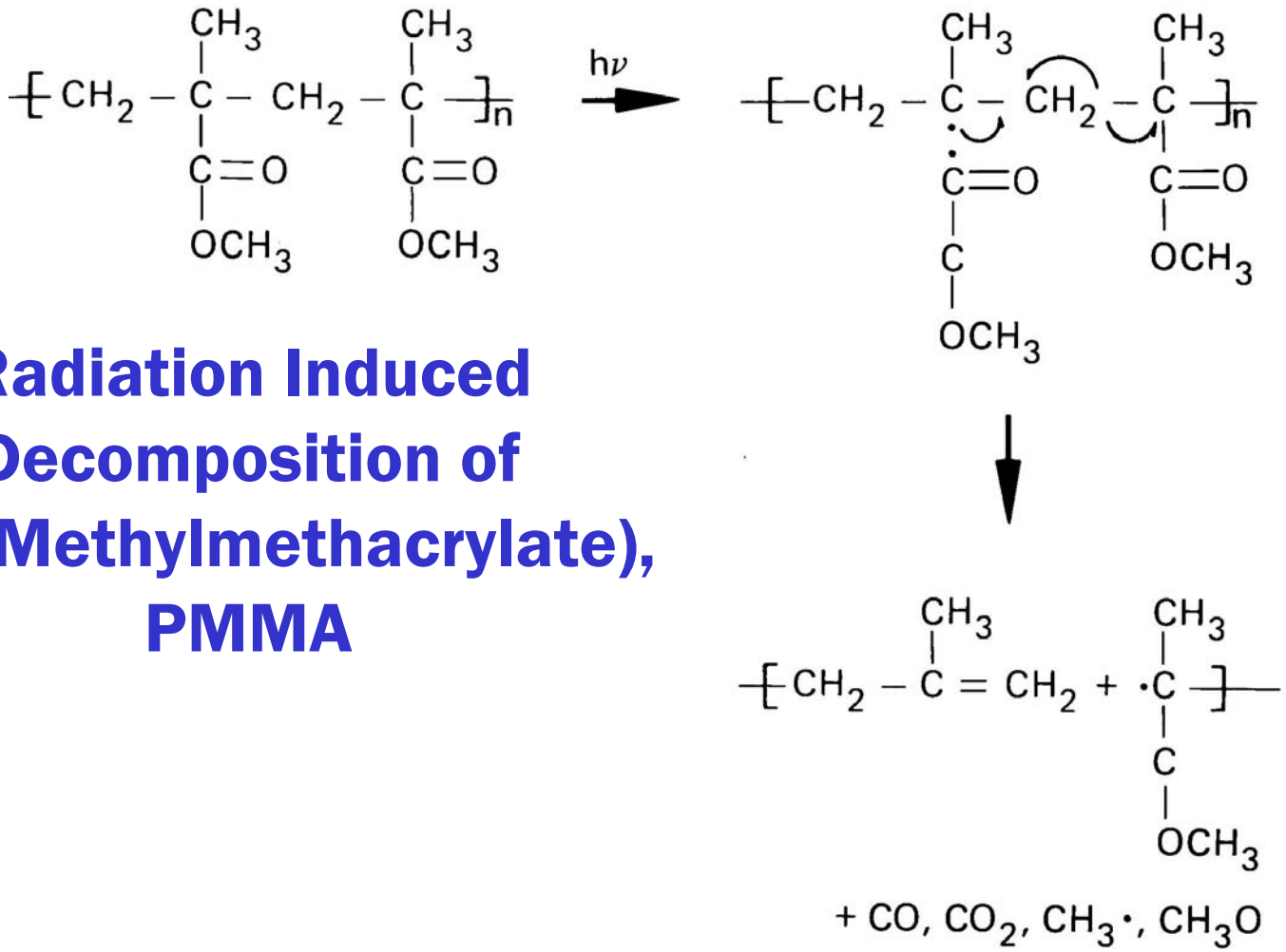
- differences in molecular weight
- differences in polarity and/or chemical reactivity towards developer

Dry development (RIE)

- differences in dry etch rate

These mechanisms can be used in both positive and negative tone

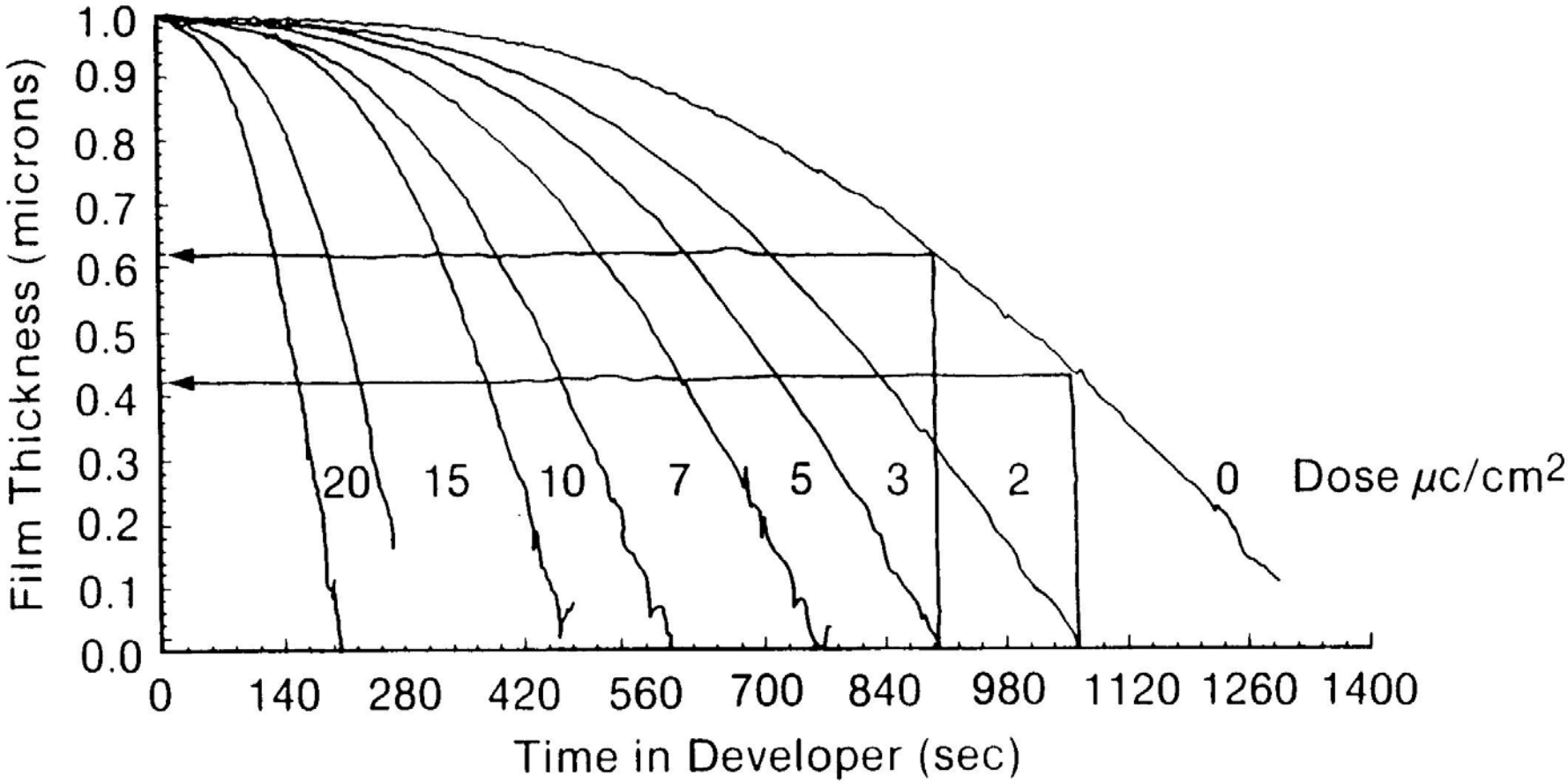
Positive tone: exposure-induced chain scission



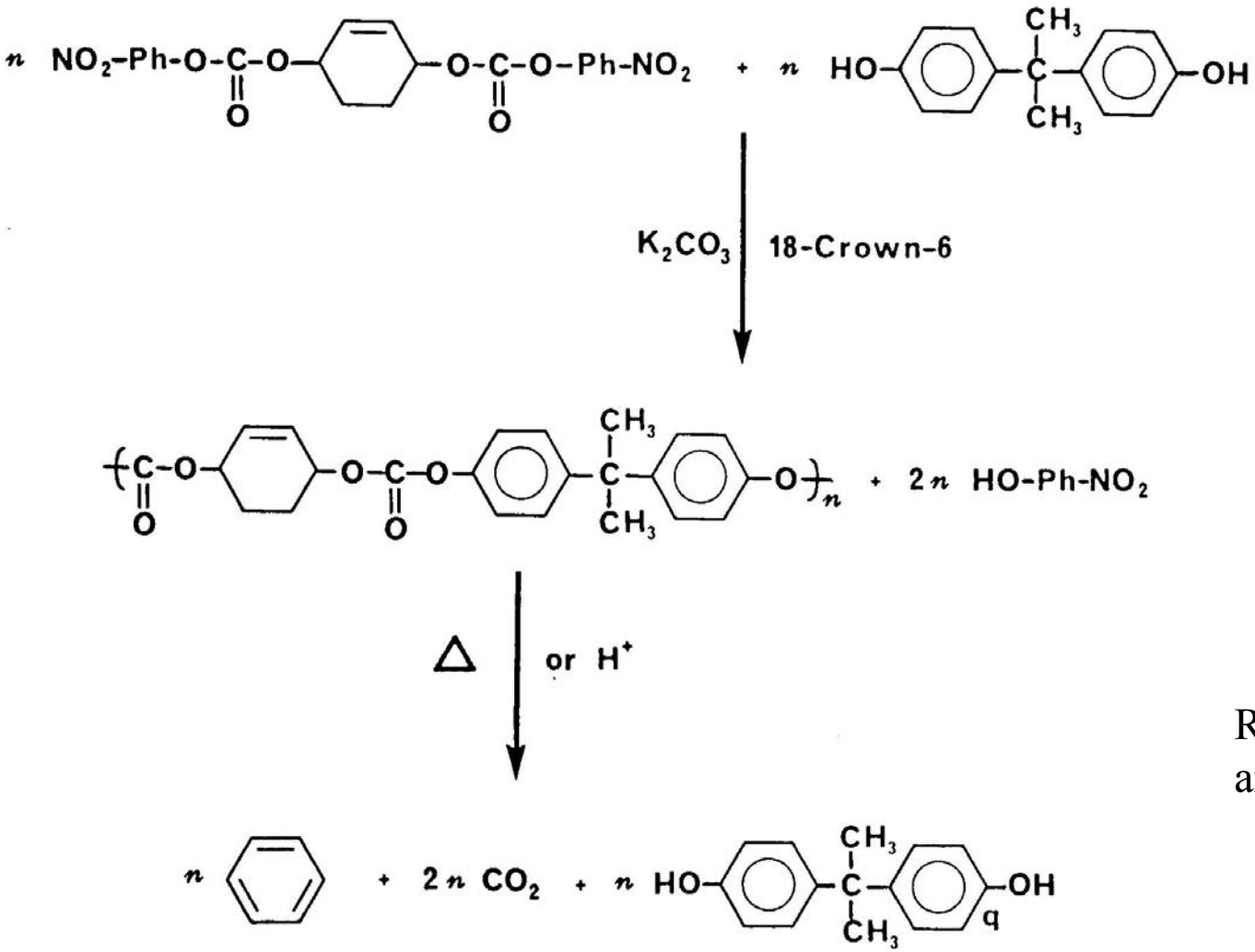
Radiation Induced Decomposition of Poly(Methylmethacrylate), PMMA

Chain scission contrast

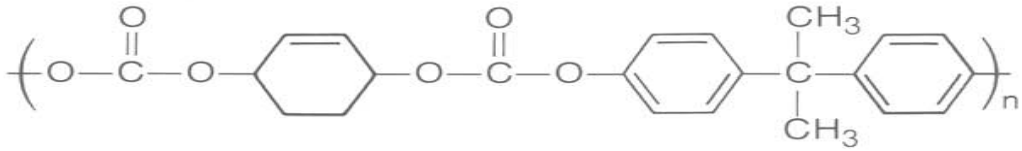
In general, dissolution rate of polymers is inversely proportional to log(MW)



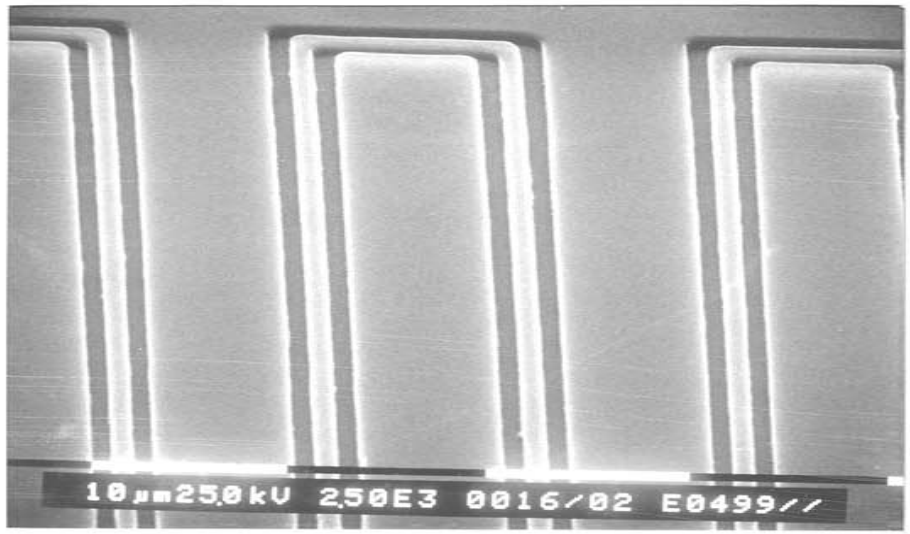
Extreme case of chain scission resist

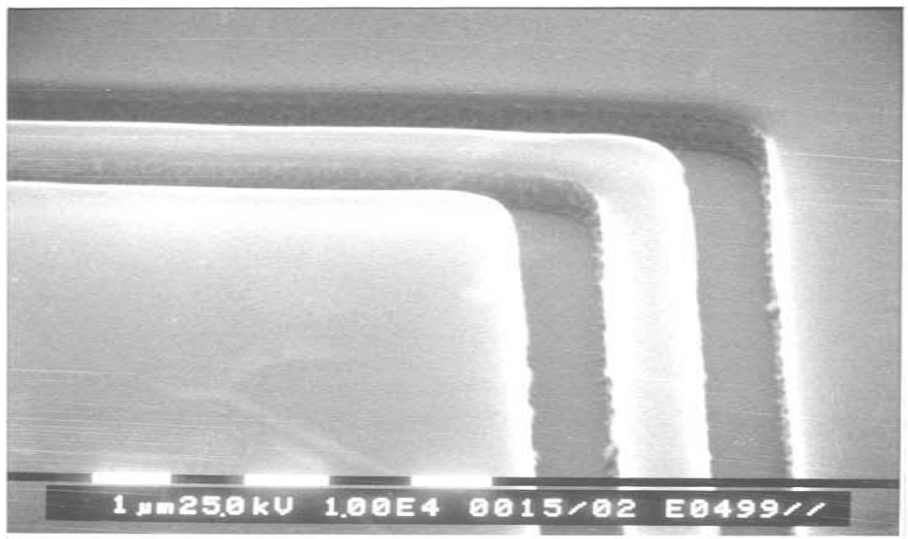


Reaction products are volatile



"Self Development"



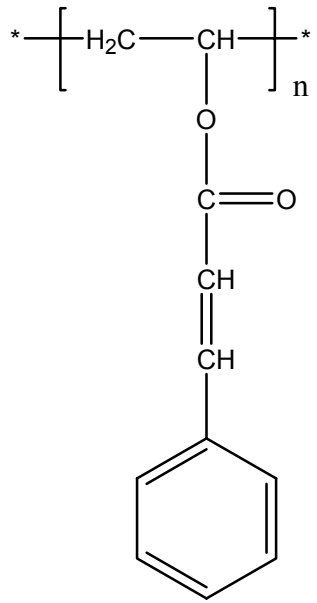


This material has very high throughput because it is CA^2, and requires no development step. Why is it not used?

Negative tone: cross-linking

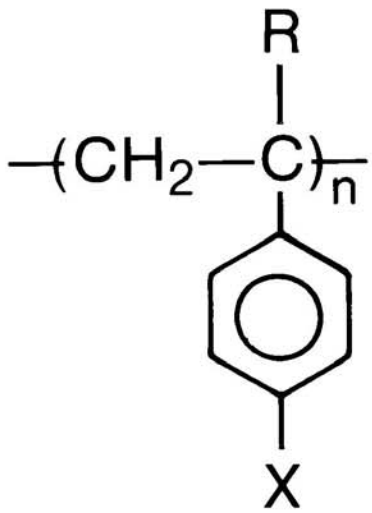
Louis Minsk
Eastman Kodak

The First Synthetic Photopolymer



Poly(vinyl cinnamate)

Single Component Negative Tone

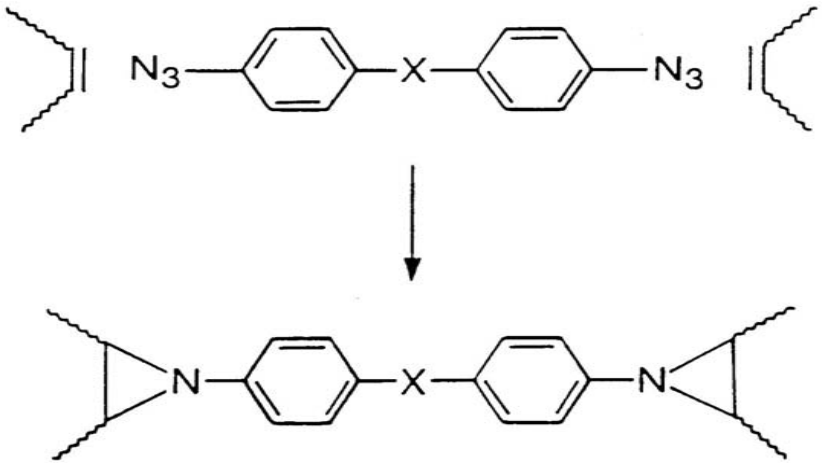
1. Polystyrenes  • Limited Resolution

$R = H,\ CH_3,\ Cl$

$X = Cl,\ -CH_2Cl$

Two Component Negative Tone

Bis-azide rubber



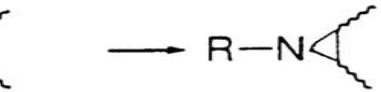
$$R{-}N_3 \xrightarrow{h\nu} R{-}N{:} + N_2$$

Azide → Nitrene + Nitrogen

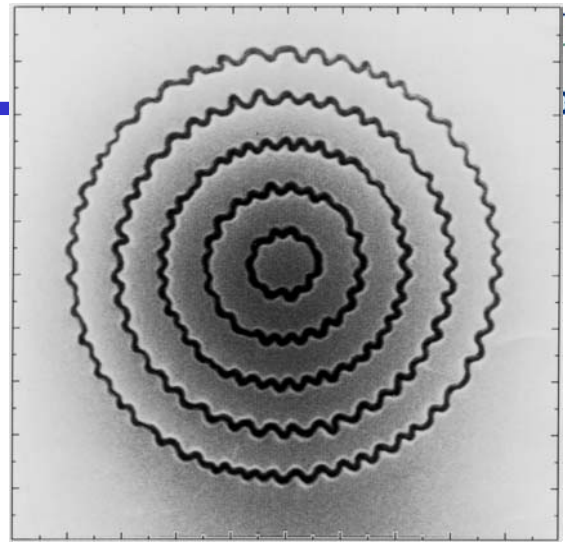
$$R{-}N{:} + R{-}N{:} \longrightarrow R{-}N{=}N{-}R$$

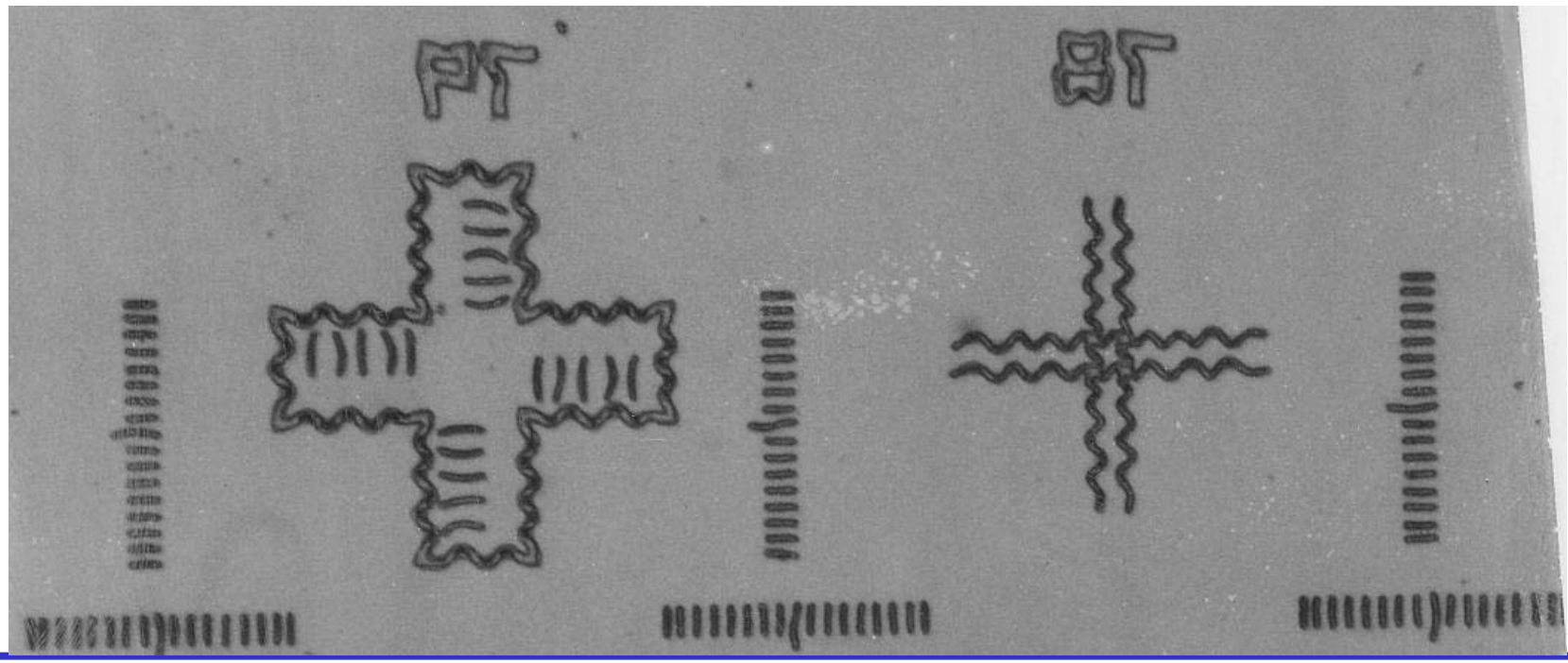
$$R{-}N{:} + H{-}\overset{|}{C}{-} \longrightarrow R{-}NH{-}\overset{|}{C}{-}$$

$$R{-}N{:} + H{-}\overset{|}{C}{-} \longrightarrow R{-}NH{\cdot} + {\cdot}\overset{|}{C}{-}$$

$$R{-}N{:} + \text{  } \longrightarrow R{-}N\text{  }$$

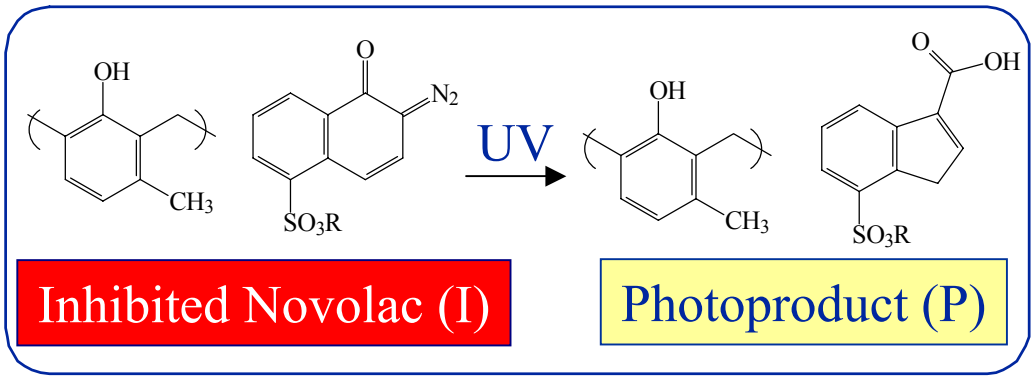
Swelling in negative tone materials

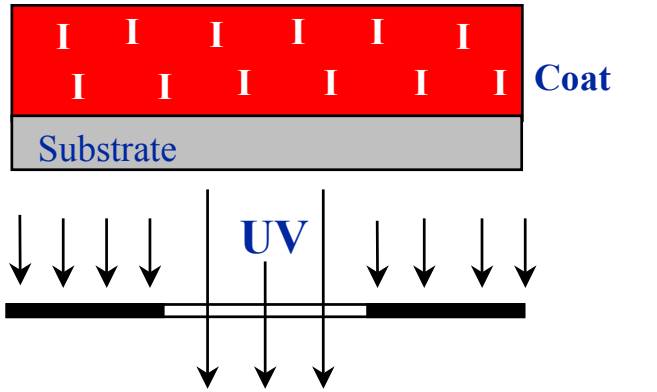


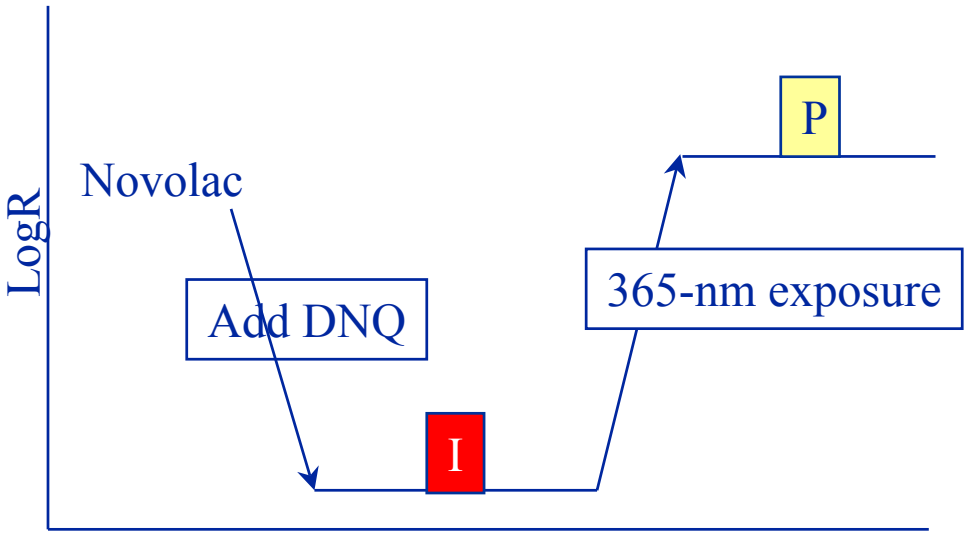


Polarity switching resists

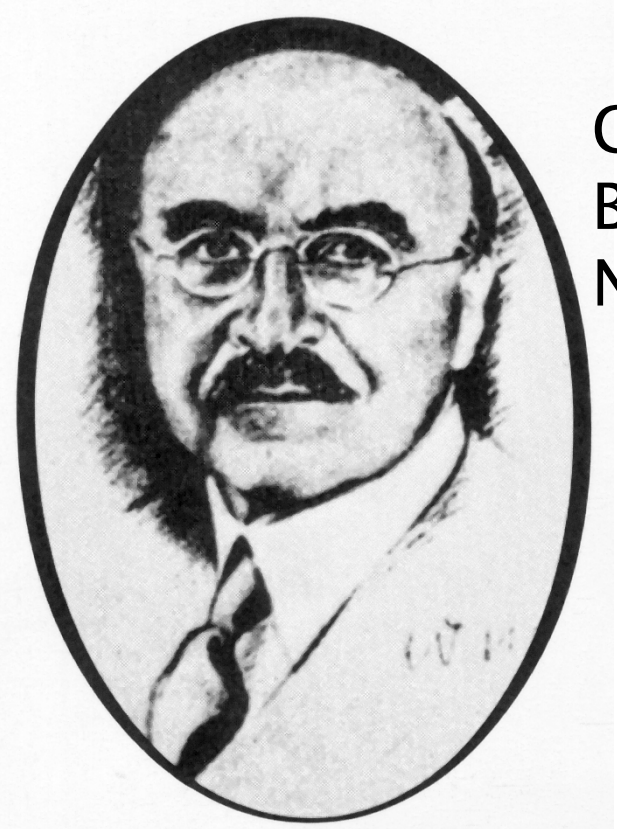
Novolac/DNQ Photoresists





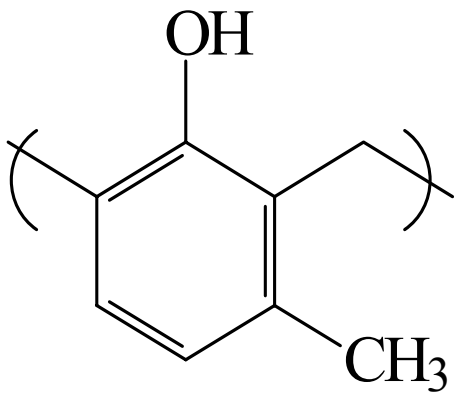


The History of Novolac



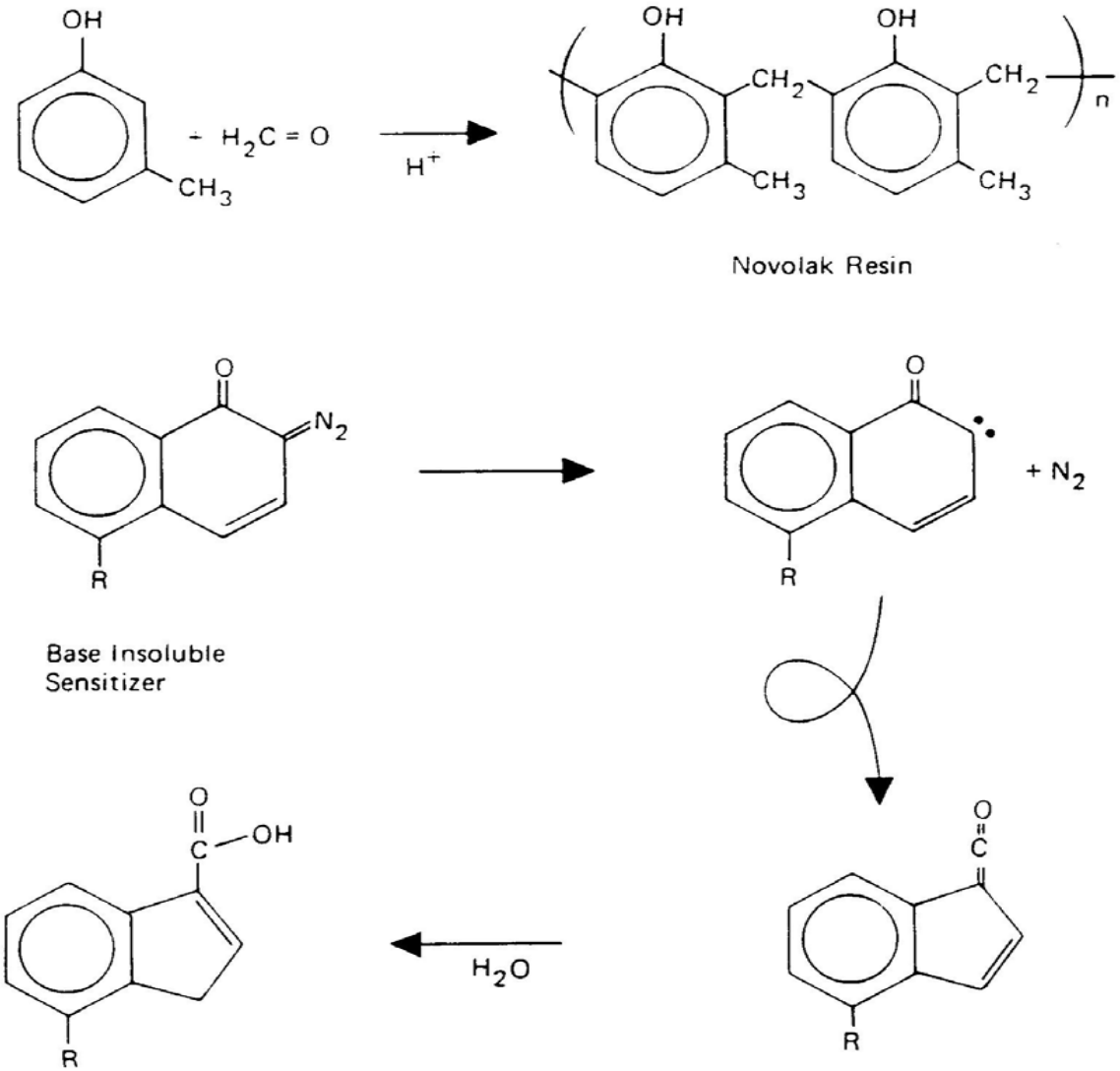
Baekeland

C.H. Meyer and L.H. Baekeland Discovered Novolac ca. 1900



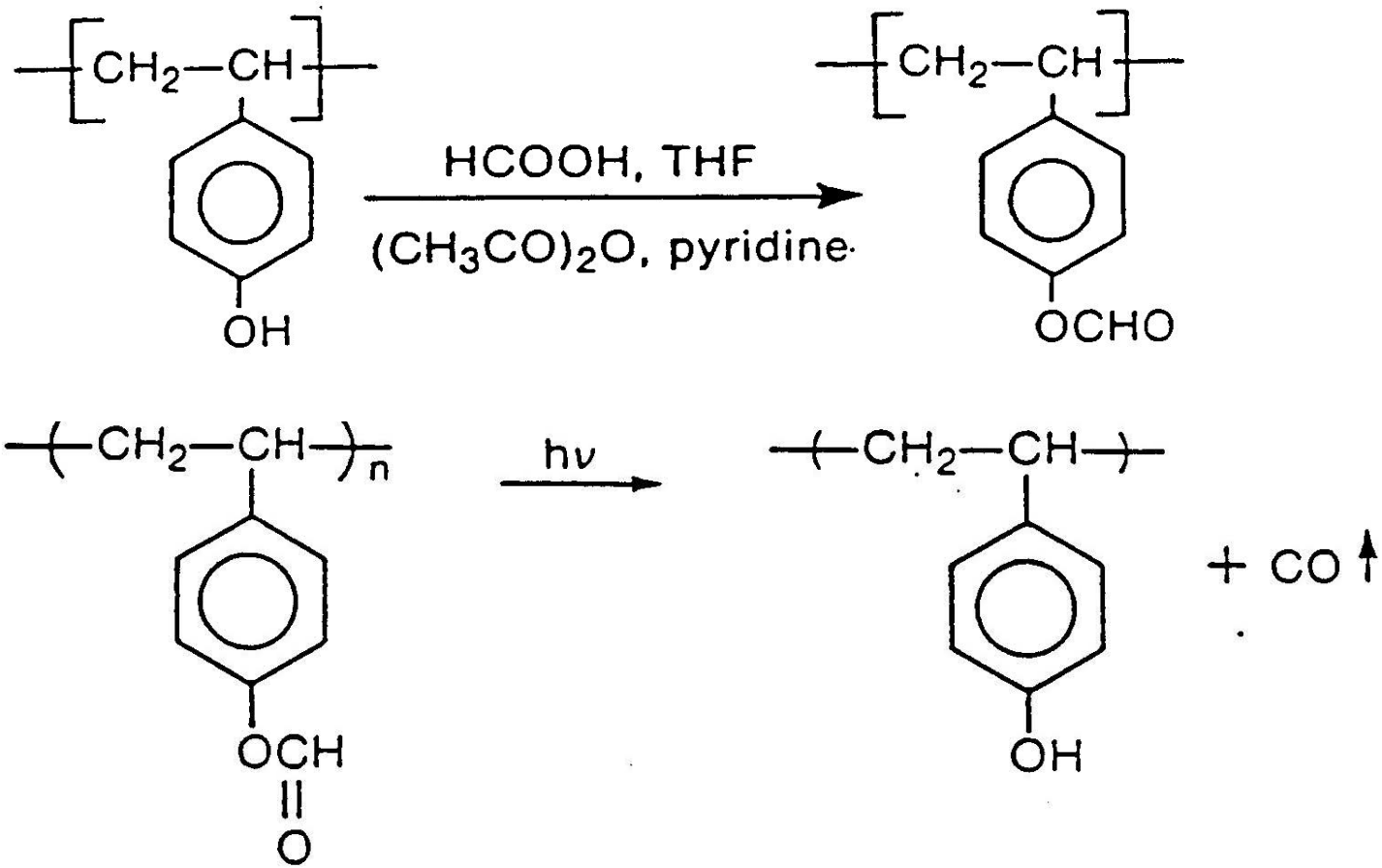
Meyer

Diazonaphthoquinone-Novolac Resists



Polarity switching resists

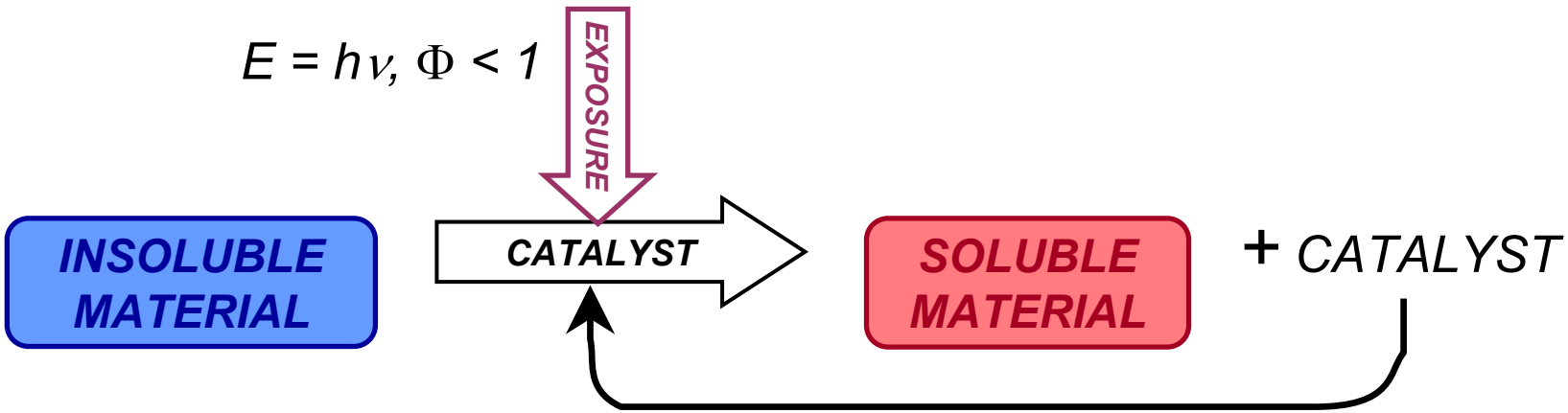
Side Chain Deprotection Design



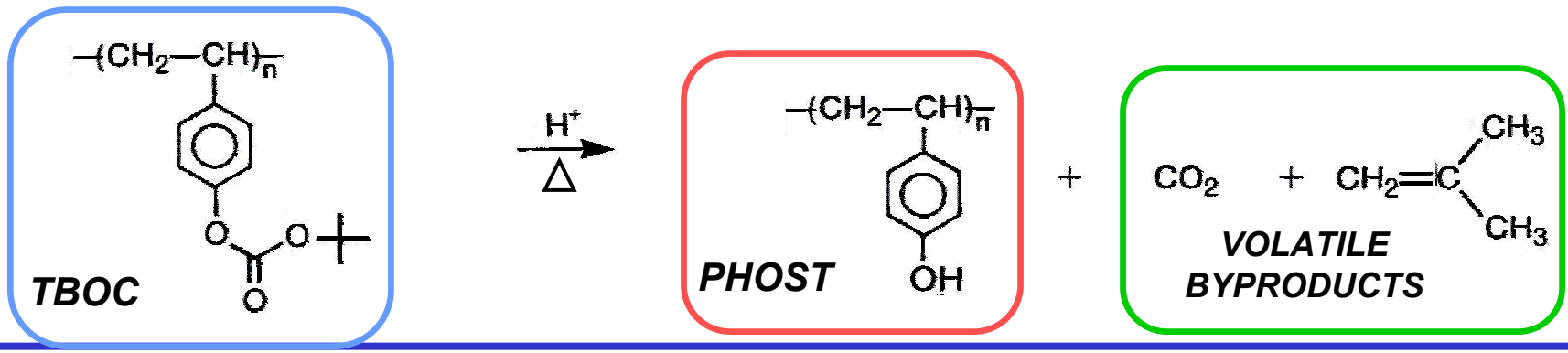
Chemical amplification

Hundreds of solubility conversion reactions per absorbed photon.

General positive-tone function:



Model system:



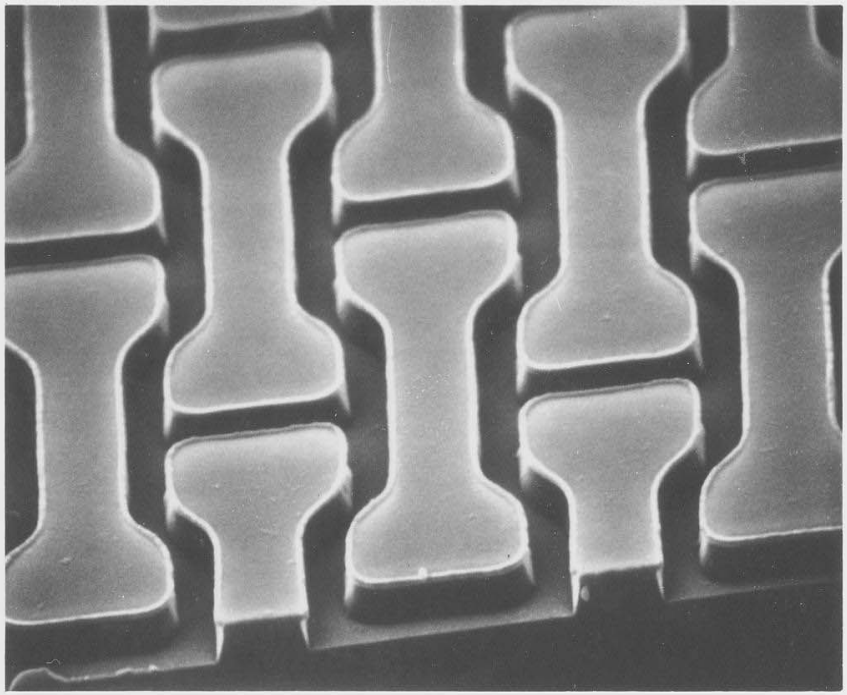
Chemical contamination in CARs

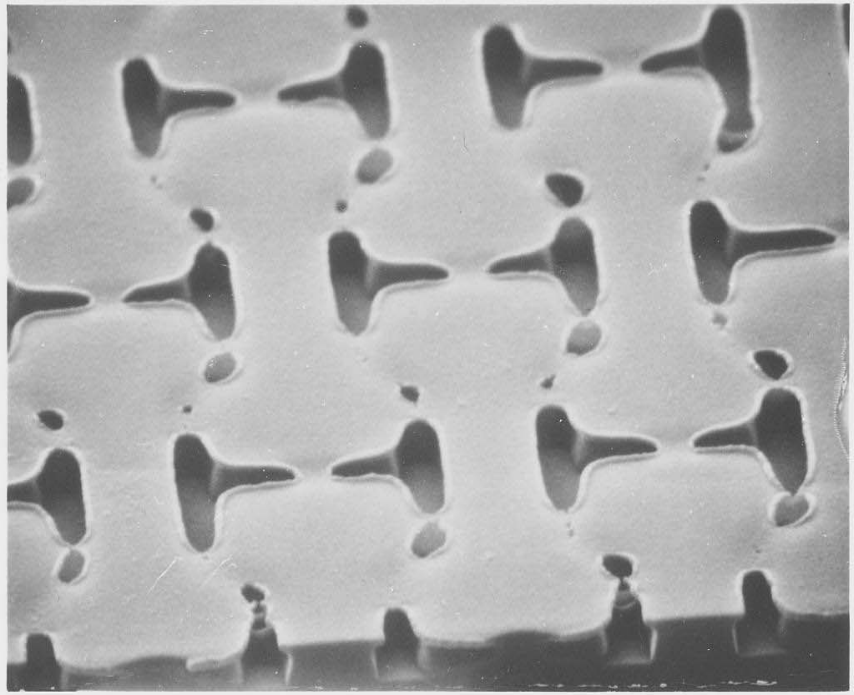
"T" tops

15 min in filtered air

15 min in 10ppb
NMP before exposure

Positive Tone Image vs. Delay Time

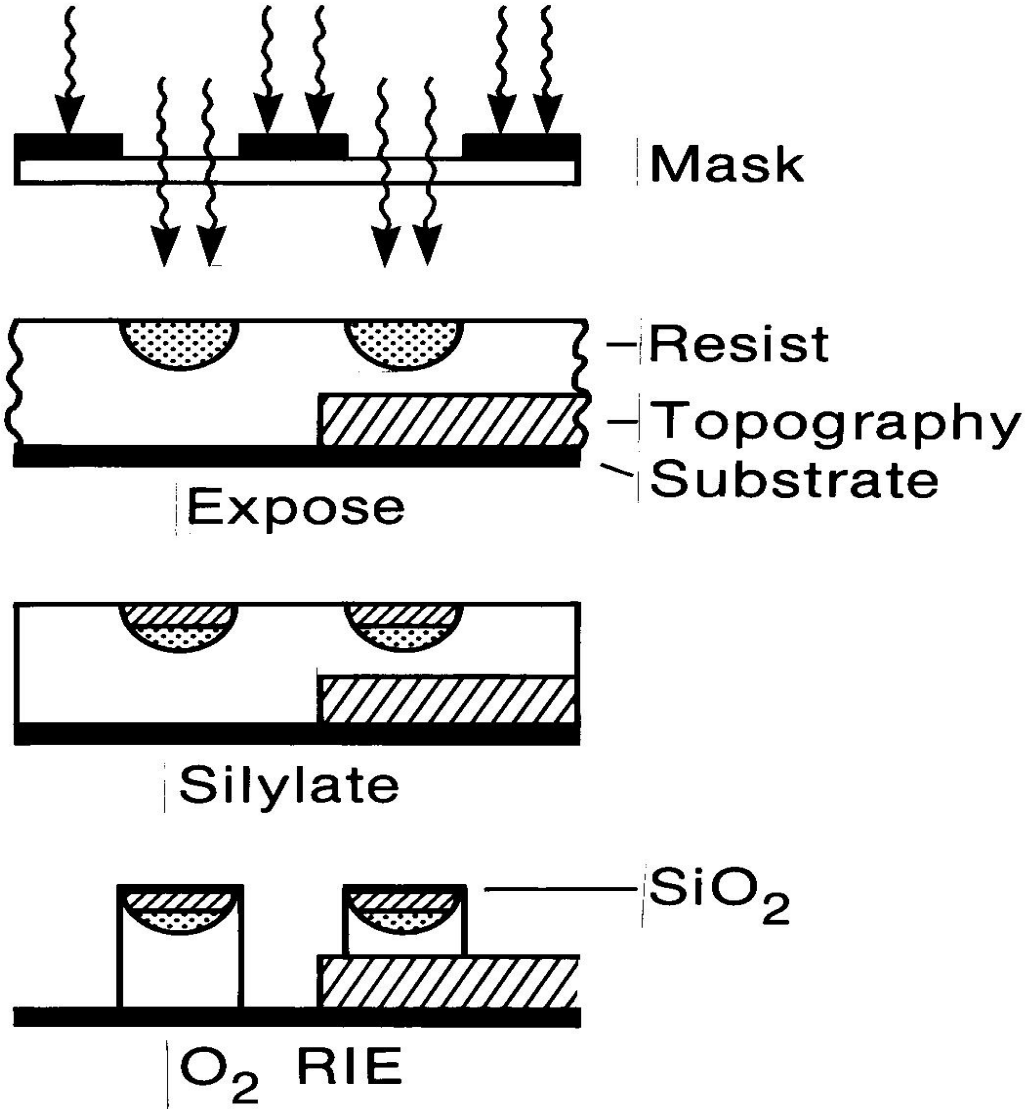




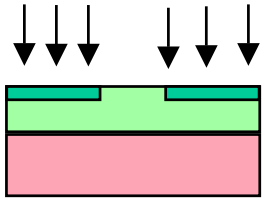
No Delay

Post Coating Delay

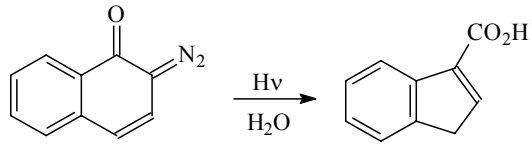
Dry development of resists

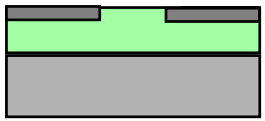


Silylation Process

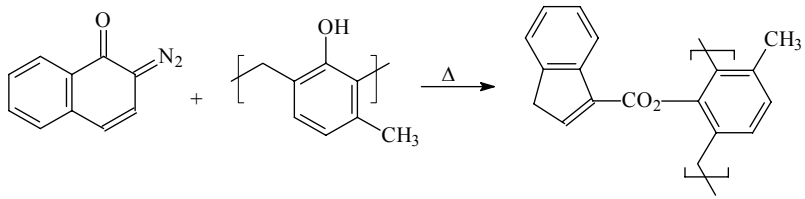


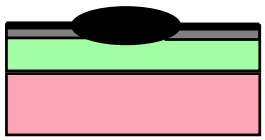
Expose



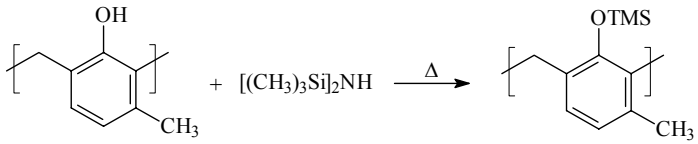


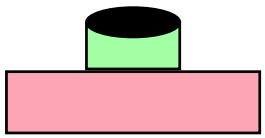
Bake



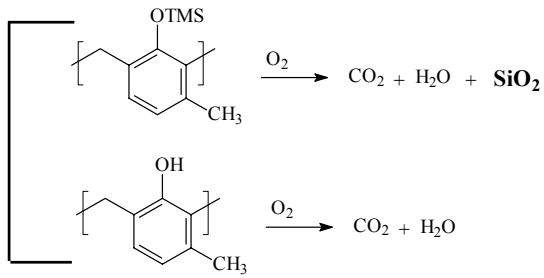


Silylate

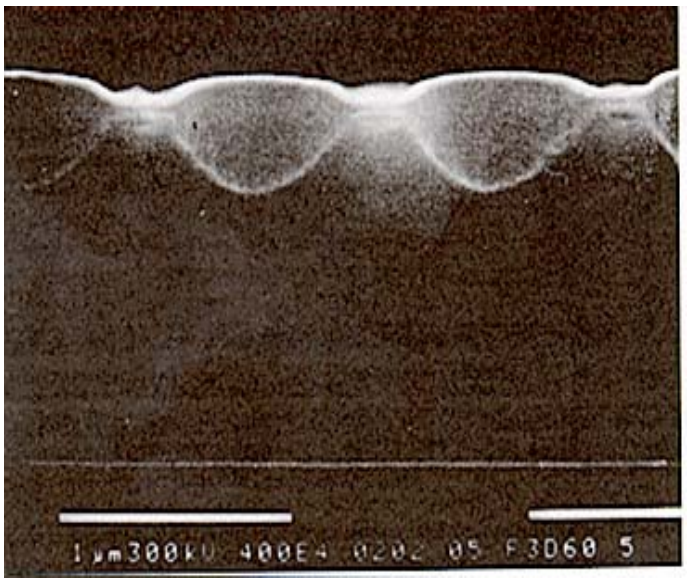


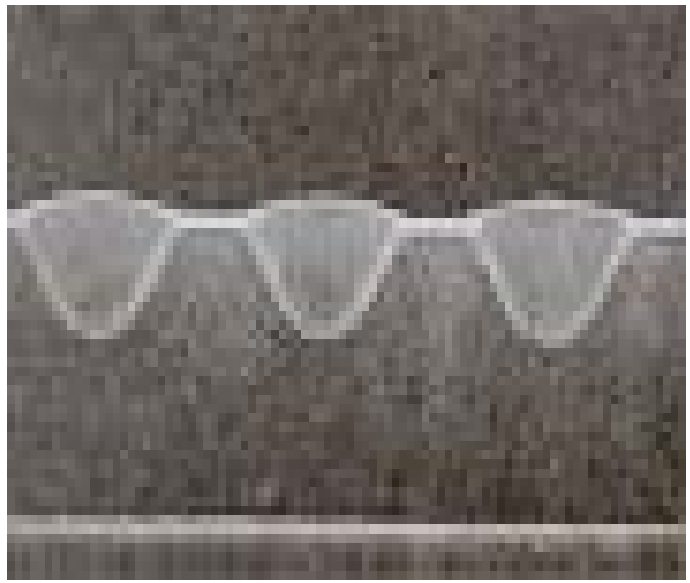


Etch

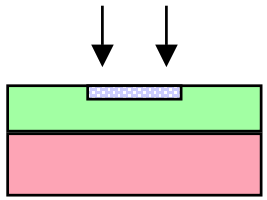


Analog Silylation Process

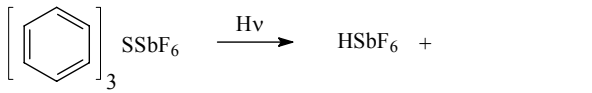


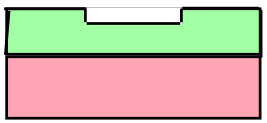


Zero Volume Change Silylation Process

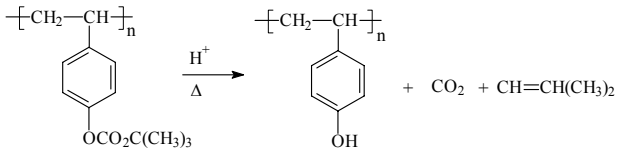


Expose

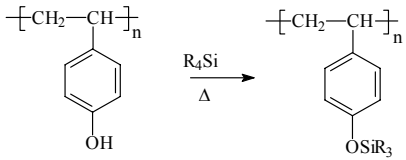


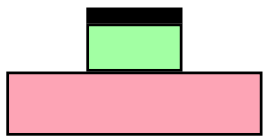


Bake

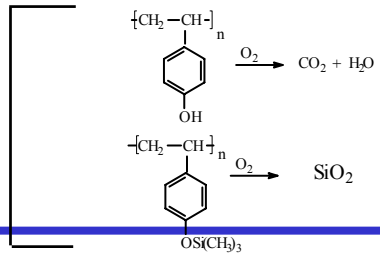


Silylate

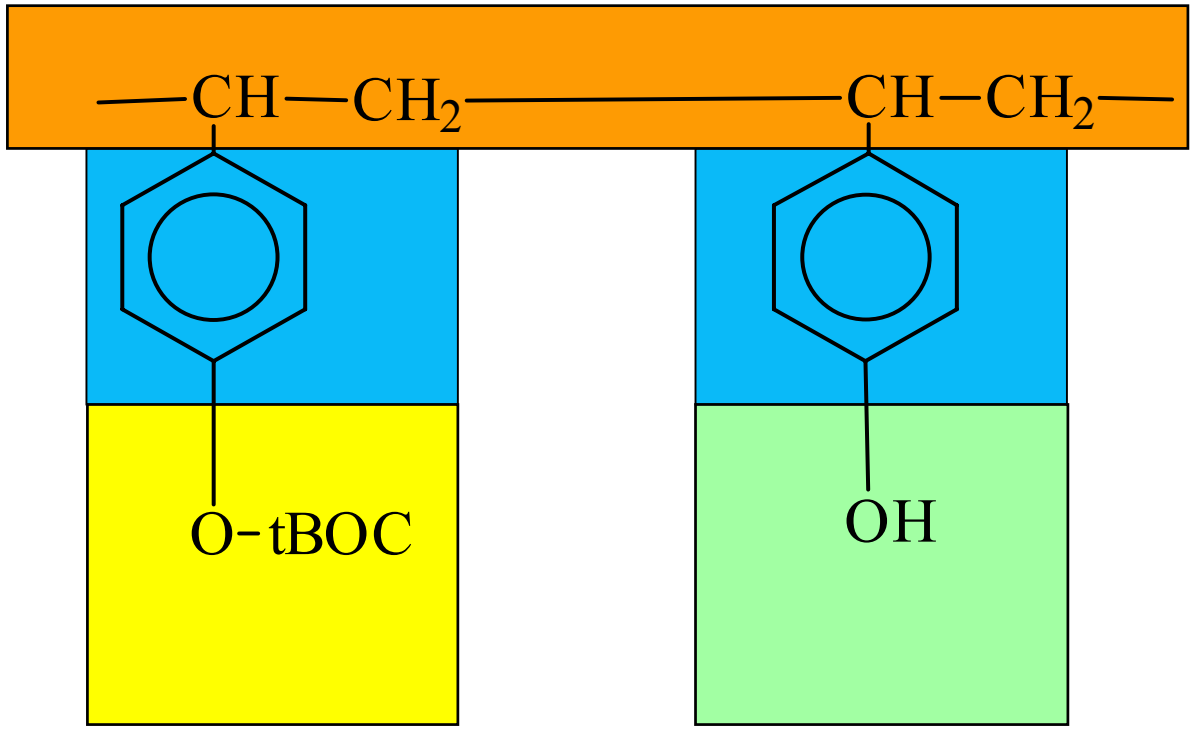




Etch



APEX Resist Design

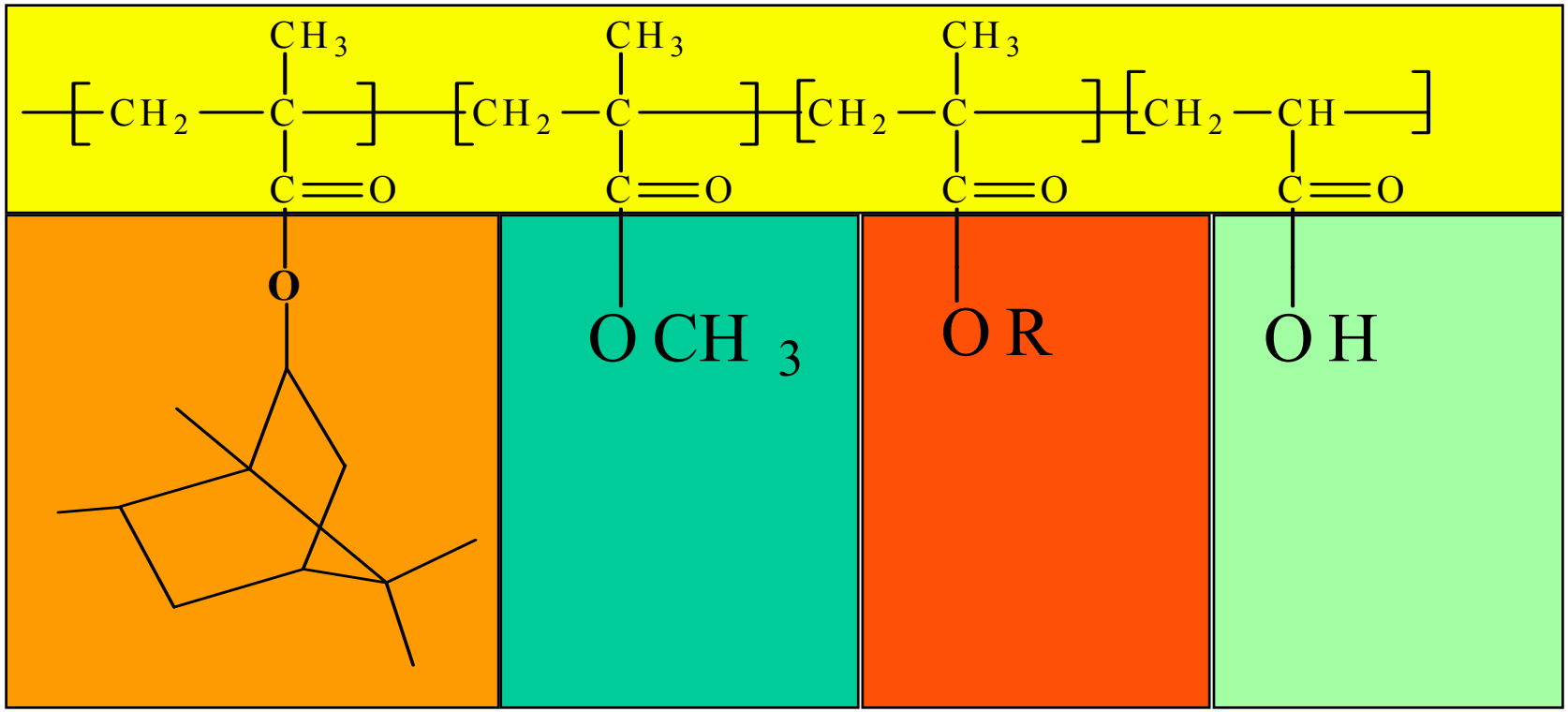


Tethering Function Acid Lability Base Solubility

Etch Resistance

Design of CARs: manufacturability

IBM Version 2 Tetrapolymer



Tethering Function Acid Lability Base Solubility

Etch Resistance Mechanical Properties

Allen, R. D., Wallraff, G. M., DiPietro, R. A., Hofer, D. C., Kunz, R. R. *Proc. SPIE*. 2438, *1995*, 474

Impact of Photoresist Absorbance on Developed Image Profile